The Acyl Effect on Intramolecular Palladium-Catalyzed Trimethylenemethane Cycloadditions

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Enhancing the generality of the intramolecular palladium-catalyzed [3 + 2] cycloaddition involving trimethylenemethane complexes as reactive intermediates is possible by incorporation of acyl substituents on the TMM unit. Such substituted TMM-PdL_2 species greatly expand the scope such that bicyclo[3.3.0]octyl, bicyclo[4.3.0]nonyl, and bicyclo[5.3.0]decyl ring systems all can be created. Furthermore, the acyl-TMM chemistry permits incorporation of a bridgehead methyl substituent—the first example of a TMM-PdL_2 cycloaddition in synthetically useful yields initiated by attack of a tertiary carbon in the first step to give a quaternary center. The requisite substrates are readily available using nucleophilic acylations via lithiated thioacetals. A general lynchpin strategy derives from bis(methylthio)methane onto which can be attached both the donor and acceptor partners of the cycloaddition. 2-((Trimethylsilyl)methyl)propenal serves as a convenient conjunctive reagent to introduce the donor partner. Alternatively 2-acyldithianes serve as a lynchpin to build substrates leading to bicycles bearing bridgehead substituents. In this case, 2-bromo-3-(trimethylsilyl)propene serves as a convenient conjunctive reagent to create the donor partner. The beneficial effect of acyl substitution derives from a combination of inhibiting side reactions derived from protodesilylation processes and facilitating the initial step of this nonconcerted cycloaddition. In addition to improving the generality of the intramolecular process, the ketone group that results in the product is a powerful functionality for further structural elaboration.

The promise offered by the intramolecular version of the palladium-catalyzed cycloadditions of trimethylenemethane (TMM) units induces us to search for ways to improve its scope.[1,2] Two approaches are feasible. The first involves the design of substrates to minimize known side reactions. The second invokes a search for a catalyst system to optimize the efficiency of the cycloaddition. Initial efforts have focused on the former strategy.

Choosing substituents to enhance the propensity for conjugate addition should promote cycloaddition since the first step of this process is a Michael-type reaction.[3] Substituents that make the nucleophilic center softer are required. In addition, minimizing protodesilylation should diminish the most important competing side reaction. Choosing an anion-stabilizing group should achieve both goals. Such a group enhances the polarizability of a nucleophile and diminishes its basicity. The versatility of the carbonyl group for further synthetic manipulations made it an obvious choice. In this paper, we report the general utility of acyltrimethylenemethane intermediates for intramolecular cycloadditions.

Preparation of Substrates

Scheme I outlines the general strategy to the requisite substrates. It derives from the ability to effect a thioacetal hydrolysis in the presence of the fully elaborated bifunctional conjunctive unit.[4,5] The ultimate source of this bifunctional unit is the aldehyde **1**, which, in turn, is readily available from the corresponding alcohol,[6] a key intermediate to the parent TMM precursor. We previously showed this aldehyde to be a very useful general precursor to monosubstituted TMM intermediates.[5]

Scheme II outlines our initial approach to two perhydroindanone precursors. Metalation of the dithiane **2b**[7] proved troublesome even with *tert*-butyllithium. Nevertheless, the sequence of metalation, carbonyl addition, quenching with methyl chlorocarbonate, and silyl ether hydrolysis produced the donor half (i.e. **3**) in 35% yield in a single operation. Following oxidation, olefination to **5** and hydroxylative Knoevenagel condensation[9] to **7** created the acceptor moieties. Gratifyingly, oxidative dithiane hydrolysis[10] proceeded uneventfully to the two substrates **6** and **8**. Spectral characteristics showed the latter to be a 1:1 diastereomeric mixture.

The difficulties in the dithiane metalation led us to examine the corresponding dimethyl thioacetal.[11] In this case, we explored a lynchpin type strategy as outlined in Scheme III. Metalation–alkylation to grow the acceptor chain as in **10** proceeded in 95% yield. Indeed, metalation (even with *n*-butyllithium), carbonyl addition, and acylation to grow the donor chain (e.g. **11**) proceeded in an overall 46% yield. The greater facility of this sequence with the acyclic thioacetal **10** compared to the cyclic thioacetal **2** led us to adopt this system for subsequent substrates. We chose to make the acetate **12** rather than a carbonate to evaluate the effect of this substituent on the cycloaddition.

The desire to incorporate bridgehead substituents, especially methyl, prompted us to build a suitable substrate beginning with alcohol **11a**. Attempts to effect oxidation under a variety of conditions led to no reaction, decomposition products, or to the elimination product **15**. On the other hand, the Dess–Martin periodinane[12] provided the desired enone in 70% yield. Unfortunately, attempts to add methyl organometallics led to 1,4- rather than

(1) For an overview, see: Trost, B. M. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1. Trost, B. M. *Pure Appl. Chem.* **1988**, *60*, 1615.
(2) Trost, B. M.; Grese, T. A.; Chan, D. M. T. *J. Am. Chem. Soc.* **1991**, *113*, 7350.
(3) Trost, B. M.; Miller, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 3687.
(4) For some recent reviews, see: Page, P. C. B.; van Niel, M. B.; Prodger, J. C. *Tetrahedron* **1989**, *45*, 7643. Grobel, B. T.; Seebach, D. *Synthesis* **1977**, 357. Lever, O. W., Jr. *Tetrahedron* **1976**, *32*, 1943.
(5) Trost, B. M.; Nanninga, T. N.; Satoh, T. *J. Am. Chem. Soc.* **1985**, *107*, 721.
(6) Trost, B. M.; Chan, D. M. T.; Nanninga, T. N. *Org. Synth.* **1984**, *62*, 58.
(7) For alcohol **2a**, see: Marius, M.; Bassery, L. *C. R. Hebd. Seances Acad. Sci., Sci. C* **1975**, *280*, 1529; *Chem. Abstr.* **1976**, *84*, 31024z. Rama Rao, R. V.; Deshmukh, M. N.; Sharma, G. V. M. *Tetrahedron* **1987**, *43*, 779.
(8) Shahak, I.; Almog, J. *Synthesis* **1970**, 145.
(9) Trost, B. M.; Grese, T. A. *J. Org. Chem.*, in press. Dominguez, E.; Carretero, J. C. *Tetrahedron Lett.* **1990**, *31*, 2487.
(10) Corey, E. J.; Erickson, B. W. *J. Org. Chem.* **1971**, *36*, 3553.
(11) Trost, B. M.; Murayama, E. *Tetrahedron Lett.* **1982**, 1047.
(12) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155.

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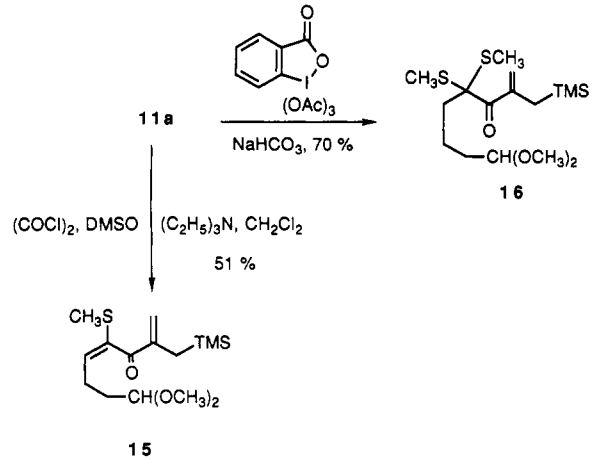
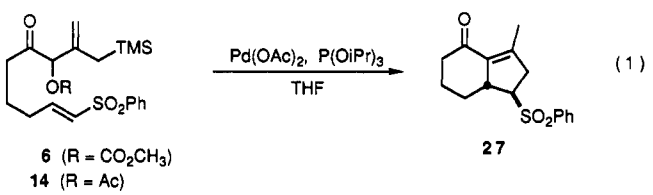


1,2-addition. To obviate this problem, the order of addition of the methyl and vinyl units was reversed as shown in Scheme IV. Addition of (1-(trimethylsilyl)-2-propenyl)lithium to ketone **17**[13] proceeded without complications of enolization. Quenching the lithium alkoxide with methyl chlorocarbonate produces the tertiary allylic carbonate **18** readily. Considering the great difficulties in forming such carbonates from the alcohols, it is remarkable how smoothly this quenching proceeds. The remaining stages via the aldehyde **19** and olefin **20** to the final substrate **21** proceeded by direct analogy to the previous routes.

To explore the applicability of this cycloaddition to other ring systems, we returned to our lynchpin strategy as outlined in Scheme V. The applicability of this sequence underscores the reliability of the dimethyl thioacetal protocol.

Cycloadditions

The intramolecular cycloaddition of carbonate **6** was explored under the standard conditions: 5% palladium(II) acetate, 30% triisopropylphosphite, 1 equiv of BSA, 0.1 M in THF, with extensive pretreatment of the substrate at 60 °C with BSA. The observation that contact of the substrate with the catalyst at room temperature (rt) induced an immediate color change (bright yellow) suggested allowing the reaction to continue at 25 °C. After 18 h, the solution had again become colorless and the reaction was complete. The ^{1}H NMR analysis of the crude reaction mixture revealed essentially a single product **27** containing no *exo*-methylene protons (eq 1). The facility of this

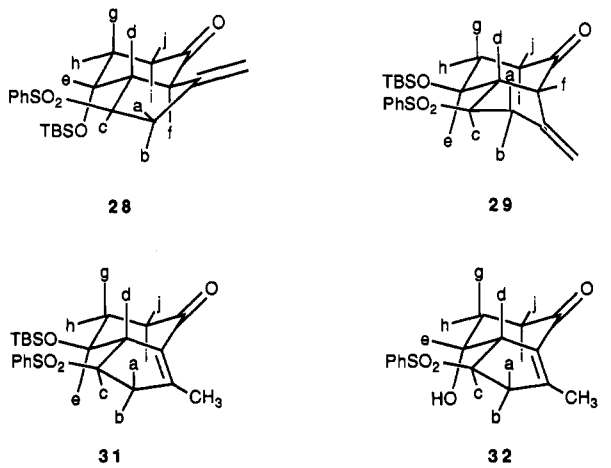


(1)

reaction, and the expectation that the carbonyl group would decrease the basicity of the TMM intermediate, implied that BSA might not be necessary. Reaction under the same conditions, but without pretreatment or addition of BSA, was complete in 5 h at rt, yielding 81% of cycloadduct **27**. Although small amounts of *exo*-methylene compounds were observed in the crude reaction mixture, these could not be isolated. The identity of the product was substantiated by infrared absorbances at 1680 and

(13) Cf Colombo, L.; Gennari, C.; Scolastico, C.; Beretta, M. G. *J. Chem. Soc., Perkin Trans.* **1978**, 1036.

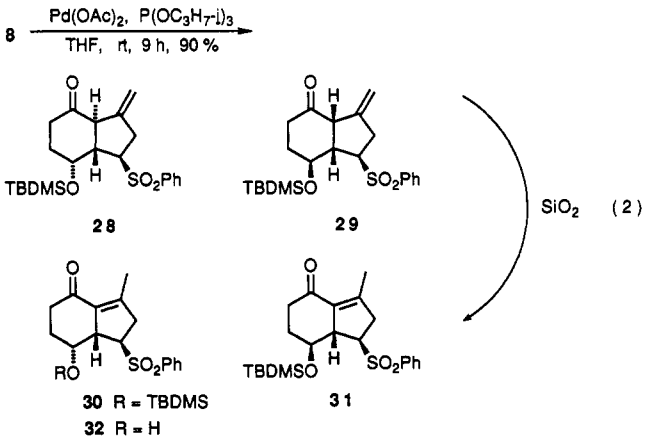
Chart I



1620 cm^{-1}, ^{13}C NMR signals at δ 198.8, 147.7, and 133.2 for the enone grouping, and a narrow doublet (1.1 Hz) at δ 1.99 in the ^{1}H NMR spectrum for the allylic methyl protons. The stereochemistry of the starting vinyl sulfone was assumed to be translated to the product based on previous results.[1]

The implication that the presence of methoxide might be responsible for the bond migration led to the investigation of acetate **14**. Surprisingly, however, its cycloaddition led to a 75% yield of the same product **27**. The reduced reactivity of the acetate required that significantly higher temperatures (dioxane, 100–110 °C) be employed.

With optimum reaction conditions established, the reaction of siloxy acceptor **8** was explored to establish the effect of the carbonyl group on the diastereoselectivity. In the event, a 2.1:7.9:2.5:1.0 mixture of four isomers **28–31**, two containing endocyclic double bonds and two containing exocyclic double bonds, was observed in the crude ^{1}H NMR spectrum (based upon intensities of *tert*-butyl resonances at δ 0.92, 0.80, 0.82, and 0.89, respectively) (eq 2).

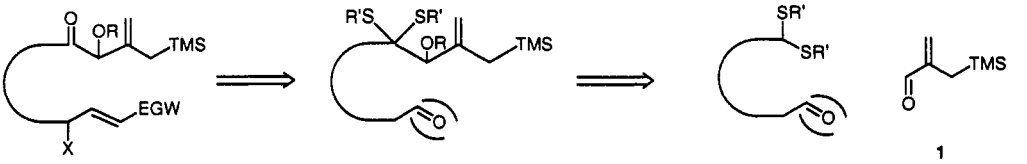


(2)

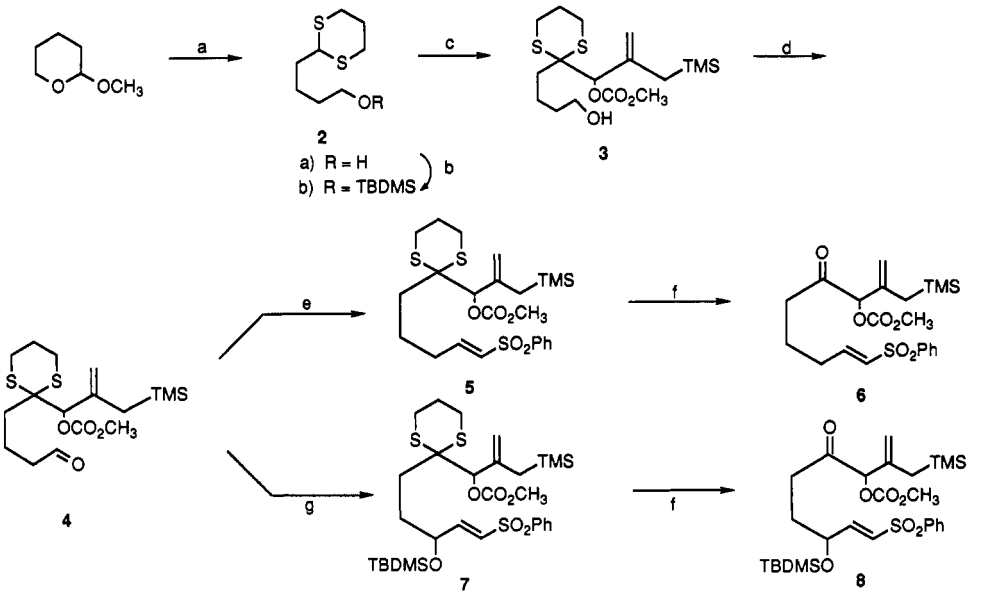
Chromatography resulted in the isolation of **28**, **31**, and a mixture of **29** and **30** in an overall ratio of 1:3.2:1.1:1 (ordered **28**, **29**, **30**, **31**) and an overall yield of 90%. This product ratio corresponds to an approximately 2:1 diastereofacial selectivity with respect to the silyloxy substituent. Desilylation of the mixture of **29** and **30** allowed isolation of alcohol **32** but resulted in decomposition of **29**.

Cycloaddition structures were assigned based upon spectroscopic data (Chart I), particularly ^{1}H NMR decoupling experiments, and the relevant signals are listed in Table I. The stereochemistry of **28** was evident by comparison with the cycloadduct lacking the carbonyl group.[2] Small coupling constants for the ^{1}H NMR signal

Scheme I

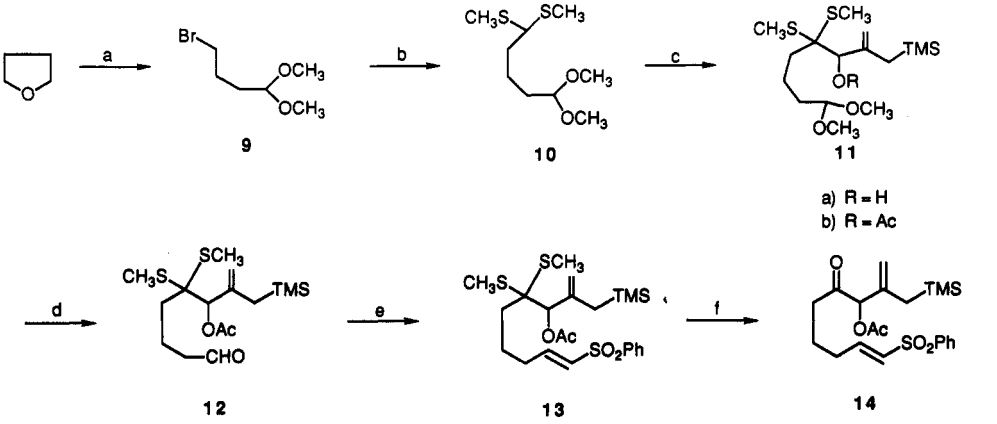


Scheme II.[a] Initial Synthesis of Perhydroindanone Precursor



[a] (a) $HS(CH_2)_3SH$, BF_3 ether, 72%; (b) TBDMS-Cl, $C_3H_4N_2$, DMAP, DMF, 95%; (c) t-C_4H_9Li, THF, 1; CH_3OCOCl; 1 N H_2SO_4; 35%; (d) PCC, Celite, CH_2Cl_2, 79%; (e) $PhSO_2CH_2P(O)(OC_2H_5)_2$, $NaN(TMS)_2$, THF, 100%; (f) NCS, $AgNO_3$, CH_3CN, H_2O, 75% for **5**, 79% for **7**; (g) (i) 4-$ClC_6H_4SOCH_2SO_2Ph$, $C_5H_{11}N$, CH_3CN, (ii) TBDMS-OSO_2CF_3, DMAP, CH_3CN; 66%.

Scheme III.[a] Lynchpin Strategy to Perhydroindanone Precursor



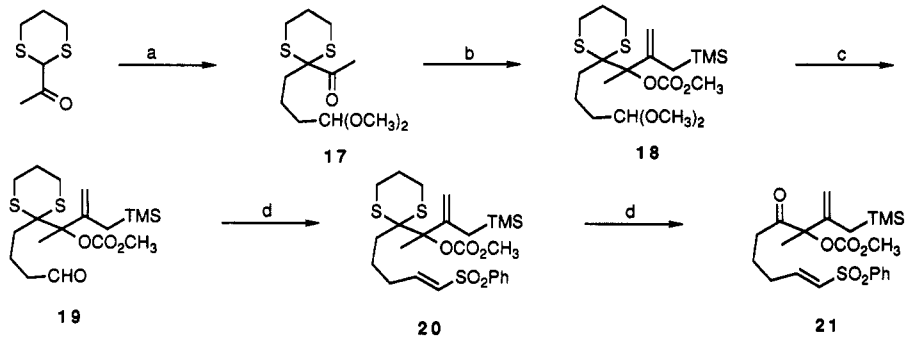
[a] (a) (i) TMS-Br, rt; (ii) PCC, Celite, CH_2Cl_2; (iii) $HC(OCH_3)_3$, CH_3OH, NH_4Cl; 35%; (b) $CH_3SCH_2SCH_3$, n-C_4H_9Li, THF, 95%; (c) (i) n-C_4H_9Li, THF, 1; (ii) Ac_2O, DMAP, C_5H_5N; 35%; (d) 1 N H_2SO_4, THF, 100%; (e) $PhSO_2CH_2P(O)(OC_2H_5)_2$, $NaN(TMS)_2$, THF, 70%; (f) NCS, $AgNO_3$, CH_3CN, H_2O, 47%.

Table I. ^{1}H NMR Data for Cycloadducts 28–32

	chemical shifts in $CDCl_3$, δ									
	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h	H_i	H_j
28	2.36	2.55	3.50	2.55	4.74	3.58	1.87	2.08	2.55	2.27
29	2.64	2.95	3.47	2.86	3.71	3.63	1.7–2.0		2.2–2.5	
31	2.55	2.91	3.65	3.51	3.76	NA	1.88	2.01	2.25	2.55
32	2.39	2.88	4.11	3.61	4.15	NA	1.94	2.07	2.56	2.33

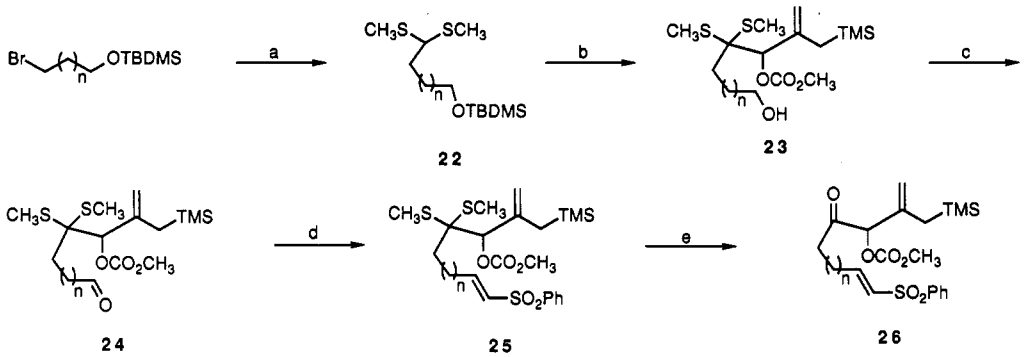
	coupling constants J (Hz)							
	a–b	a–c	b–c	c–d	d–e	d–f	e–g	e–h
28	17.0	9.5	9.8	9.8	small	13.6	small	
n29	18.4	8.0	4.6	4.8	8.2	8.0	8.2	3.7
31	19.1	9.9	5.2	5.0	8.6	NA	8.6	4.8
32	17.7	9.5	9.3	8.9	2.7	NA	small	

Scheme IV.[a] Construction of Perhydroindanone Precursor via Ketodithiane



[a] (a) NaH, $I(CH_2)_3CH(OCH_3)_2$, DME, 56%; (b) t-C_4H_9Li, $CH_2{=}C(Br)CH_2TMS$, $ClCO_2CH_3$, ether, 62%; (c) 1 N H_2SO_4, THF, 96%; (d) $PhSO_2CH_2P(O)(OC_2H_5)_2$, $NaN(TMS)_2$, THF, 81%; (e) NCS, $AgNO_3$, CH_3CN, H_2O, 44%.

Scheme V.[a] Generalization of Lynchpin Strategy



[a] (a) $CH_3SCH_2SCH_3$, n-C_4H_9Li, THF, n = 1 or 3, 95%; (b) n-C_4H_9Li, THF, 1, CH_3OCOCl; H_2SO_4, H_2O; n = 1, 44%, n = 3, 35%; (c) PCC, Celite, CH_2Cl_2, n = 1, 64%, n = 3, 78%; (d) $PhSO_2CH_2P(O)(OC_2H_5)_2$, $NaN(TMS)_2$, THF, n = 1, 85%, n = 3, 81%; (e) $AgNO_3$, NCS, CH_3CN, H_2O, n = 1, 81%, n = 3, 62%.

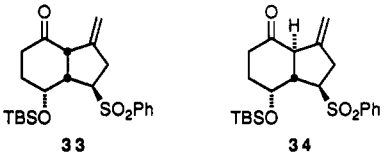
at δ 4.74 as well as its downfield shift indicated an equatorial proton adjacent to the silyloxy group and syn to the phenyl sulfone (H_e).[14] A 13.6-Hz coupling constant for a doublet at δ 3.58, assigned as H_f, implied a trans ring fusion. Olefinic signals at δ 5.48 and 5.05 were appropriate for the *exo*-methylene unit.

The structure of **31** was apparent from the absence of olefinic signals in the ^1H NMR spectrum and the allylic methyl singlet at δ 1.88 as well as the enone infrared absorbances at 1689 and 1635 cm^{-1}. The stereochemistry was assigned based on the 8.6-Hz triplet coupling constant for H_e at δ 3.76 signalling two trans-diaxial couplings. This information can only be accommodated by a proton trans to both the bridgehead proton and the phenyl sulfone, assuming the starting olefin geometry was translated to product stereochemistry.

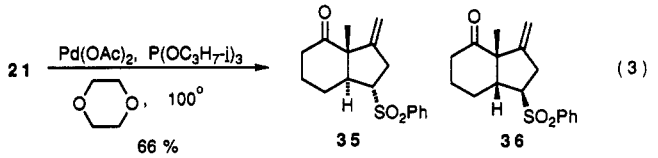
The structure of the desilylated cycloadduct **32** (derived from **30**) was indicated by enone infrared absorbances at 1684 and 1629 cm^{-1} and a narrow doublet (1.3 Hz) for the allylic methyl at δ 2.01 in the ^1H NMR spectrum. The equatorial orientation of H_e was evidenced by its expression as a broad singlet at δ 4.15.

Finally, the stereochemistry of **29** was deduced by its conversion, upon prolonged exposure to silica gel, to **31**. An 8.0-Hz coupling constant for the doublet at δ 3.63 in the ^1H NMR spectrum indicated a cis ring juncture.

It is curious that cycloadducts **33** and **34** have not been detected. Rapid isomerization under the reaction conditions to endocyclic olefin isomers **30** and **31**, respectively, may account for this observation. At this point, the much higher rate of cycloaddition with these carbonyl substituted TMM intermediates relative to the simple alkyl system must be noted.



The beneficial effect of the carbonyl group translated to the methyl-substituted analogue **21**. Exposing the latter to the standard conditions required 100 °C in dioxane but gave a gratifying 66% yield of the perhydroindanones **35** and **36** in a 2.4:1 ratio (eq 3). This result contrasts with



(3)

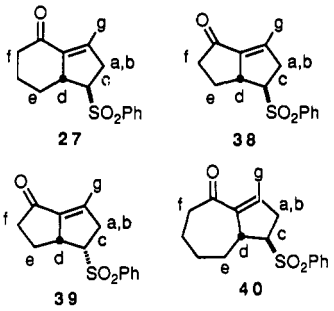
a 33% yield for the substrate lacking the carbonyl group.[2] The product ratio was determined from integration of the methyl singlets at δ 1.14 (major) and δ 1.35 (minor) in the ^1H NMR spectrum. The relative stereochemistry was assigned based on analogy to other bridgehead-substituted hydrindanes wherein the trans isomer shows the absorption for the methyl substituent at higher field.[15]

The angle strain introduced by incorporating a carbonyl group in the tether leading to a bicyclo[3.3.0]octyl system

(14) Trost, B. M.; Seoane, P.; Mignani, S.; Acemoglu, M. *J. Am. Chem. Soc.* **1989**, *111*, 7487. Schmuff, N. R. Ph.D. Thesis, University of Wisconsin, Madison, WI, 1985.

(15) Piers, E.; Marais, P. C. *J. Org. Chem.* **1990**, *55*, 3454. Lansbury, P. T.; Briggs, P. C.; Demmin, T. R.; Du Bois, G. E. *J. Am. Chem. Soc.* **1971**, *93*, 1311.

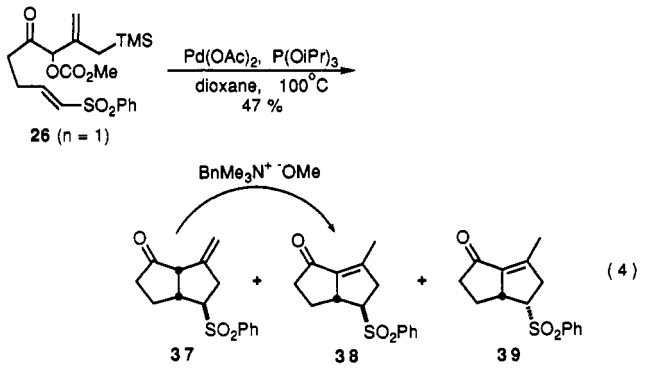
Table II. ^{1}H NMR Chemical Shifts Comparison for Methylcyclopentene Cycloadducts



27 38 39 40

	chemical shifts in $CDCl_3$, δ					
	H_a, H_b	H_c	H_d	H_e	H_f	H_g
27	2.44, 2.95	3.53	3.39	1.46, 1.28	2.44, 2.16	1.99
38	2.74, 3.42	3.69	3.63	1.84, 1.36	2.42	2.00
39	3.00	3.96	3.73	2.4, 2.22	2.6	2.00
40	2.59, 2.91	3.31	3.51	1.8, 1.4	2.47	1.99

should make the cycloadditions of **26** (n = 1) more difficult than the perhydroindanone ring formation.[16] Indeed, this cycloaddition required 100 °C in dioxane and gave a 5.4:2.0:1.0 ratio of **37**:**38**:**39** (eq 4). The chromatographic

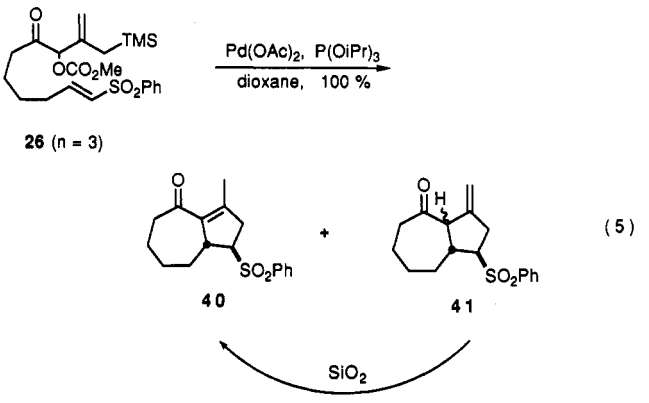


(4)

separation of **37** from **38** was extremely difficult and allowed isolation of only an analytical sample of **37**. Cycloadduct **38** was isolated from the base-catalyzed isomerization of its mixture with **37**; however, this resulted in substantial decomposition.

The enone products were indicated by infrared absorbances at 1709 and 1659 cm^{-1} for **38** and 1712 cm^{-1} for **39**, as well as allylic methyl singlets at δ 2.00 in their ^{1}H NMR spectra. The stereochemistry of **38** was assigned based on previous results, indicating that cycloaddition products of (*E*)-olefins generally reflect the stereochemistry of the starting material. A comparison of chemical shifts for the protons adjacent to the bridgehead (H_e in Table II) showed a considerable downfield shift for **39**, consistent with that expected for a methylene unit syn to the phenyl sulfone.[14] The stereochemistry of **37** follows from its conversion to **38**. In this case, the cis ring junction is assumed due to the strain involved in formation of the *trans*-bicyclo[3.3.0]octane system.[17]

The possibility of forming of a perhydroazulene provides a major test of the effect of an acyl group on the intramolecular TMM reactions since cycloadditions of the parent hydrocarbon failed.[2] Exposing substrate **26** (n = 3) to the usual catalyst of 5% palladium(II) acetate and 30% triisopropyl phosphite in dioxane at 100 °C initially gave an 8.2:1 mixture of **40** and **41** in 51% yield (eq 5).



(5)

Repeated chromatography allowed isolation of **40** in 47% yield presumably because of isomerization of **41** upon exposure to silica gel. Infrared absorbances at 1676 and 1616 cm^{-1} were indicative of the enone structure, and a narrow doublet (1.4 Hz) at δ 1.99 in the ^{1}H NMR spectrum was assigned to the allylic methyl group of **40**. The presence of **41** in the initial product mixture was inferred from four ^{1}H NMR multiplets at δ 5.08, 5.05, 4.91, and 4.87 assigned to the *exo*-methylene protons of cis and trans ring juncture isomers.

Discussion

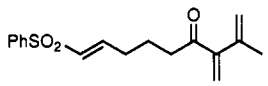
The beneficial effects of the acyl group on the intramolecular palladium-catalyzed [3 + 2] TMM reactions are clearly illustrated by the cycloadditions reported herein. Lower reaction temperatures in the case of the perhydroindanones and successful cycloadditions with a 4-atom tether, which failed in the substrate lacking the carbonyl group, attest to this. The source of this effect is difficult to pinpoint since many steps are involved in the overall catalytic cycle (see Scheme VI). We can consider the sequence to be divided into two phases: phase 1 corresponds to creation of the reactive intermediate and phase 2 to the cycloaddition of this reactive intermediate. Rate differences would be expected for the generation phase between substrates consisting of only a hydrocarbon tether (X = H_2) and a tether bearing a carbonyl group (X = O). However, it is not obvious that the latter substrates should ionize more rapidly. More significantly, no appreciable rate differences for the generation phase should be expected for acyl substrates **6**, **26** (n = 1), and **26** (n = 3), yet the temperatures required for the cycloaddition differ by about 80 °C. It would appear that the crucial aspect for the success of this overall reaction lies more in the second phase than the first.

Accordingly, the beneficial effect of the acyl group most likely lies in facilitating the conjugate addition of the TMM–PdL_2 segment. By making the donor "softer", it is a better partner for the soft Michael acceptor. This difference appears sufficient to overcome the sluggishness of the substrate bearing a 5-atom tether to cyclize, the first example of a [3 + 2] cycloaddition to create a perhydroazulene skeleton.

The acyl effect extends this intramolecular [3 + 2] cycloaddition to bridgehead substituted bicycles—a common structural type of many targets. The higher temperature required for the methyl-substituted substrate **21** compared to the parent **6** also supports the conclusion that the success of this sequence depends upon the factors controlling the cycloaddition phase of Scheme VI. The higher steric demands of the attacking nucleophile slows the conjugate addition step, thereby requiring the higher

(16) Cf Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 5699.
(17) Baneth, J. W.; Linstead, R. P. *J. Chem. Soc.* **1935**, 436. Engler, E. M.; Andose, J. D.; Schleyer, P.v.R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. Bailey, W. F.; Khanoldar, A. D. *Tetrahedron Lett.* **1990**, *31*, 5993.

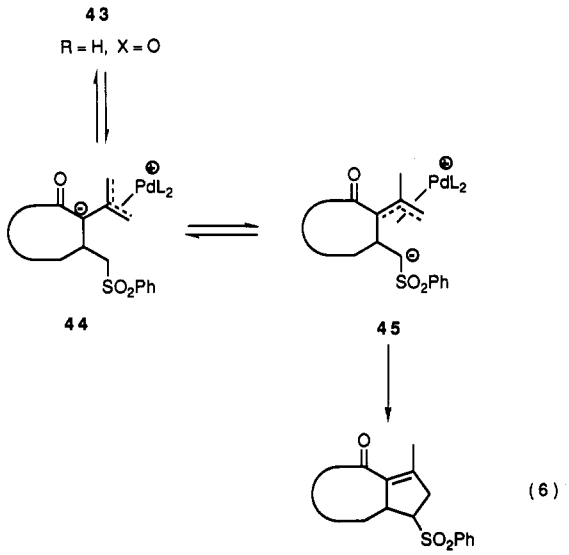
temperature. Nevertheless, the role of the acyl group would appear to be more than facilitating the conjugate addition. In this case, elimination to products like **42**



42

would have been anticipated to form competitively with the cycloaddition. The lower basicity of the TMM–PdL_2 intermediate should disfavor such processes. The success of the cycloaddition of **21** may be attributed to both effects: facilitation of the desired reaction and disfavoring potential competing reactions.

The formation of the endocyclic olefin products at first glance would appear to arise by simple base-catalyzed isomerization of the initial products. However, an alternative mechanism cannot be ruled out (eq 6). The intermediate after the first bond formation (Scheme VI, **43**, R = H) possesses a very acidic hydrogen. As a result, it may equilibrate with an alternative π-allyl intermediate **45** either by a series of intramolecular proton transfers as represented by the intermediate **44** or by intermolecular proton transfers. The failure to detect appreciable amounts of the exocyclic olefin isomer in eq 1 may derive from this alternative pathway competing more favorably with the direct cyclization of **43**. While this route necessitates a 5-*endo-trig* type of cyclization,[18] a few examples of such cyclizations involving π-allylpalladium intermediates have been described.[19] Generation of a TMM–PdL_2 species by deprotonation has been observed when the TMM precursor bears a strong acidifying group[20]—an observation in support of this pathway.



The introduction of a carbonyl group conjugated to the TMM–PdL_2 segment greatly expands the range of ring systems and substitution patterns possible via intramolecular cycloadditions. The thioacetal strategy allows ready construction of substrates with great flexibility. As a multibond-forming process in which structural complexity is increased rapidly, it should prove useful in designing synthetic strategy to polycyclic systems.

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(19) Ahmar, M.; Cazes, B.; Gore, J. *Tetrahedron* **1987**, *43*, 3453.
(20) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, 5183.

Experimental Section[21]

Preparation of 2-(4-Hydroxybutyl)-2-(1-((methoxycarbonyl)oxy)-2-((trimethylsilyl)methyl)-2-propenyl)-1,3-dithiane (3). Dithiane **2b**[7] (4.6 g, 15 mmol) in 150 mL of THF cooled to −78 °C was treated with 10.6 mL of a 1.41 M solution of *tert*-butyllithium (15 mmol) in pentane. The bright yellow mixture was warmed gradually to 0 °C over a 3-h period, cooled to −78 °C, and treated with aldehyde **1** via cannula, rinsing the flask and cannula with an additional 2 mL of THF. When the yellow color had been dispersed, the mixture was warmed to 0 °C and stirred for 1 h. Methyl chloroformate (2.84 g, 2.33 mL, 30 mmol) was added, and the mixture was allowed to warm to rt overnight. The solution was poured into 600 mL of ether and washed with 200 mL of saturated aqueous sodium bicarbonate, and the aqueous layer was extracted with two 50-mL portions of ether. The combined organic extracts were dried over magnesium sulfate and filtered, and the solvents were removed in vacuo.

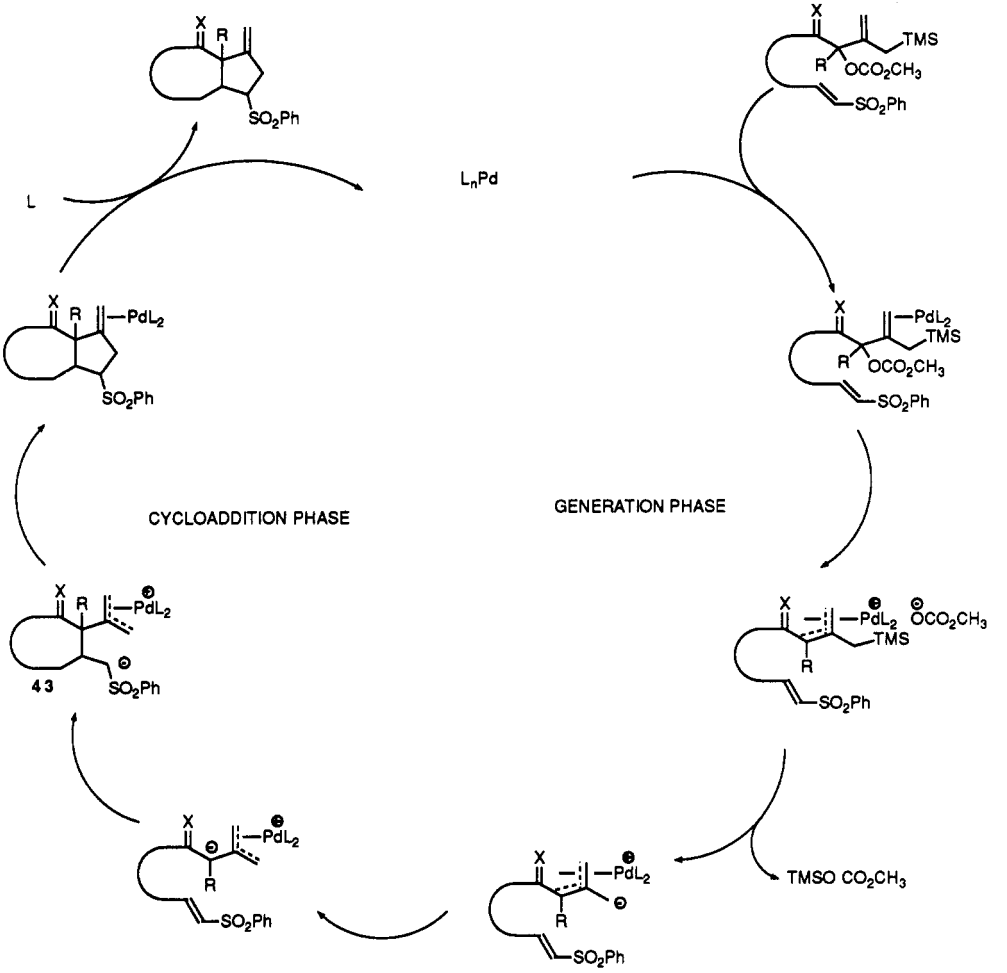
The crude product, dissolved in 75 mL of THF, was treated with 20 mL of 1 N sulfuric acid at rt for 16 h. The mixture was diluted with 400 mL of ether and washed with 50 mL of saturated aqueous sodium chloride, and the aqueous layer was extracted with two 50-mL portions of ether. The combined organic extracts were dried over magnesium sulfate and filtered, and the solvent was removed in vacuo. Flash chromatography (silica gel, 3:1 hexane–ethyl acetate) with rechromatography of the mixed fractions yielded 2.1 g (35%) of the titled compound as a clear, light yellow oil: IR ($CDCl_3$): 3620, 1740, 1630, 1460, 1450, 1430, 1270, 1170, 850 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.50 (s, 1 H), 5.04 (s, 1 H), 4.86 (s, 1 H), 3.77 (s, 3 H), 3.62 (q, J = 6.1 Hz, 2 H), 3.09 (ddd, J = 11.4, 8.5, 3.6 Hz, 1 H), 3.01 (ddd, J = 11.2, 8.4, 3.2 Hz, 1 H), 2.65 (m, 2 H), 2.05 (m, 1 H), 1.5–1.9 (m, 9 H), 1.2 (t, J = 5.6 Hz, 1 H), 0.03 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9, 141.6, 114.2, 80.6, 62.0, 55.9, 54.5, 34.8, 32.5, 26.4, 26.1, 25.2, 23.7, 20.3, −1.8. Mass: calcd for $C_{15}H_{28}OS_2Si$ (M − CH_3OCO_2H)$^+$ 316.1351, found 316.1355.

Preparation of 2-(4-Oxobutyl)-2-(1-((methoxycarbonyl)oxy)-2-((trimethylsilyl)methyl)-2-propenyl)-1,3-dithiane (4). To a stirred suspension of the above alcohol **3** (1.0 g, 2.55 mmol) and Celite (1.3 g) in 6.5 mL of methylene chloride was added PCC (841 mg, 3.9 mmol) at rt. After 2 h, the orange suspension had become dark brown and was then diluted with 10 mL of ether and treated with anhydrous sodium sulfate. After 10 min additional stirring, the slurry was filtered through a short pad of silica gel, eluting with hexane. Removal of the solvent in vacuo gave 783 mg (79%) of the titled product as a clear, colorless oil. IR ($CDCl_3$): 1740, 1720, 1620, 1440, 1420, 850, 800 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.72 (t, J = 1.7 Hz, 1 H), 5.48 (s, 1 H), 5.02 (s, 1 H), 4.94 (s, 1 H), 3.76 (s, 3 H), 3.06 (ddd, J = 14.4, 11.3, 3.1 Hz, 1 H), 2.98 (ddd, J = 14.2, 111.1, 3.1 Hz, 1 H), 2.68 (dt, J = 14.8, 4.4 Hz, 1 H), 2.63 (dt, J = 14.9, 4.4 Hz, 1 H), 2.40 (t, J = 7.0 Hz, 2 H), 1.7–2.1 (m, 8 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.6, 155.2, 141.8, 114.6, 80.7, 56.0, 54.8, 43.8, 34.6, 26.7, 26.4, 25.7, 23.8, 17.3, −1.6. Mass: calcd for $C_{15}H_{26}OS_2Si$ (M − CH_3OCO_2H)$^+$ 314.1195, found 314.1195.

Preparation of 2-((*E*)-5-(Phenylsulfonyl)-4-pentenyl)-2-(1-((methoxycarbonyl)oxy)-2-((trimethylsilyl)methyl)-2-propenyl)-1,3-dithane (5). Diethyl ((phenylsulfonyl)methyl)-phosphonate[8] (672 mg, 2.3 mmol) in 5 mL of THF was added slowly to a solution of sodium bis(trimethylsilyl)amide (418 mg, 2.3 mmol) in 10 mL of THF at −78 °C. After 1 h, the above aldehyde **4** (783 mg, 2.0 mmol) in 5 mL of THF was added slowly. After an additional 45 min at −78 °C, the mixture was poured into 120 mL of ether and 120 mL of saturated aqueous ammonium chloride. The organic layer was washed with 60 mL of water, and the aqueous layers were extracted with 60 mL of ether. The combined organic extracts were dried over magnesium sulfate and filtered, and the solvent was removed in vacuo. Flash chromatography (silica gel, 2:1 hexane–ether) gave 1.1 g (100%) of the

(21) For a general experimental section, see ref 2. Unless otherwise stated, spectroscopic and chromatographic analyses establishes the chemical purity of reported substances as ≥95%.
(22) Peterson, J. S.; Töteberg-Kaulen, S.; Rapoport, H. *J. Org. Chem.* **1984**, *49*, 2948. Vedejs, E.; Arnost, M. J.; Hagen, J. P. *J. Org. Chem.* **1979**, *44*, 3230. Ihara, M.; Takahashi, T.; Shimizu, N.; Ishida, Y.; Sudow, I.; Fukumoto, K.; Kametani, T. *J. Chem. Soc. Perkin Trans. 1* **1989**, 529.

Scheme VI



titled product as a clear, colorless oil. IR ($CDCl_3$): 1740, 1620, 1440, 1420, 1140, 1080, 1010, 850 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (dd, J = 7.0, 1.6 Hz, 2 H), 7.5–7.7 (m, 3 H), 6.96 (dt, J = 15.0, 6.3 Hz, 1 H), 6.31 (d, J = 15.1 Hz, 1 H), 5.47 (s, 1 H), 4.96 (s, 1 H), 4.90 (s, 1 H), 3.77 (s, 3 H), 3.03 (m, 2 H), 2.63 (m, 2 H), 2.20 (m, 2 H), 2.05 (m, 1 H), 1.6–1.9 (m, 7 H), 0.04 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.7, 146.2, 141.5, 140.5, 133.0, 130.6, 129.0, 127.3, 114.0, 80.1, 55.5, 54.4, 34.1, 31.0, 26.3, 26.0, 25.4, 23.4, 22.0, −1.9. Mass: calcd for $C_{22}H_{32}O_2S_3Si$ (M − CH_3OCO_2H)$^+$ 452.1334, found 452.1334.

Preparation of (*E*)-1-(Phenylsulfonyl)-6-oxo-7-((methoxycarbonyl)oxy)-8-((trimethylsilyl)methyl)-1,8-nonadiene (6). The dithiane **5** (1.06 g, 2.0 mmol) in 5 mL of acetonitrile was added to a stirred slurry of NCS (1.07 g, 8 mmol) and silver nitrate (1.53 g, 9 mmol) in 26 mL of acetonitrile containing 6.5 mL of water. A voluminous precipitate formed, and the reaction was complete almost instantaneously. The mixture was stirred for 10 min, treated successively with 3 mL of saturated aqueous sodium sulfite, 3 mL of saturated aqueous sodium bicarbonate, and 3 mL of saturated aqueous sodium chloride, and poured into 60 mL of 1:1 hexane–methylene chloride. The biphasic mixture was filtered through Celite, rinsing the filtercake with 1:1 hexane:methylene chloride. The layers were separated, and the aqueous layer was washed with 20 mL of 1:1 hexane–methylene chloride. The combined organic extracts were dried over magnesium sulfate and filtered, and the solvent was removed in vacuo. Flash chromatography (silica gel, 4:1 hexane–ethyl acetate) yielded 660 mg (75%) of the titled product as a clear, yellow oil. IR ($CDCl_3$): 1750, 1730, 1630, 1440, 1150, 1080, 1000, 850 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, J = 7.8 Hz, 2 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.52 (t, J = 7.5 Hz, 2 H), 6.92 (dt, J = 15.1, 7.2 Hz, 1 H), 6.31 (d, J = 15.2 Hz, 1 H), 5.13 (s, 1 H), 5.06 (s, 1 H), 4.91 (s, 1 H), 3.78 (s, 3 H), 2.49 (dt, J = 7.0, 4.2 Hz, 2 H), 2.20 (q, J = 6.8 Hz, 2 H), 1.70 (m, 2 H), 1.47 (s, 2 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.8, 155.1, 145.9, 140.7, 139.6, 133.4, 131.3, 129.4, 127.7, 114.5, 85.2, 55.0, 35.9, 30.1, 21.9, 20.8, −1.7. Mass: calcd for $C_{20}H_{27}O_6SSi$ (M − CH_3)$^+$ 423.1297, found 423.1293. Anal. Calcd for $C_{21}H_{30}O_6SSi$: C, 57.50; H, 6.91. Found: C, 57.52; H, 7.09.

Preparation of 2-((*E*)-5-(Phenylsulfonyl)-3-((*tert*-butyldimethylsilyl)oxy)-4-pentenyl)-2-(1-((methoxycarbonyl)oxy)-2-((trimethylsilyl)methyl)-2-propenyl)-1,3-dithane (7). The aldehyde **4** (614 mg, 1.57 mmol) was dissolved in 2 mL of acetonitrile and added slowly to a stirred solution of ((4-chlorophenyl)sulfinyl)methyl phenyl sulfone[9] (519 mg, 1.65 mmol) and piperidine (141 mg, 163 μL, 1.65 mmol) in 6 mL of acetonitrile. The mixture was stirred at rt until reaction was complete (1.5 h), diluted with 50 mL of ether, and washed with 20 mL of water. The aqueous layer was extracted with an additional 50 mL of ether, and the combined organic layers were washed with 10 mL of 10% aqueous sodium hydroxide. After drying over magnesium sulfate and filtration, the solvents were removed in vacuo. The oil was purified via flash chromatography (silica gel, 2:1 hexane–ethyl acetate) to give 732 mg (86%) of a foamy, yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ 7.88 (dd, J = 7.2, 1.7 Hz, 2 H), 7.61 (t, J = 6.8 Hz, 1 H), 7.53 (t, J = 7.4 Hz, 2 H), 6.96 (dd, J = 14.9, 3.6 Hz, 1 H), 6.58 (dd, J = 14.8, 1.4 Hz, 1 H), 5.46 (s, 1 H), 4.99 (s, 0.5 H), 4.97 (s, 0.5 H), 4.92 (s, 1 H), 4.39 (bs, 1 H), 3.77 (s, 3 H), 3.02 (m, J = 12.4 Hz, 2 H), 2.64 (m, J = 13.0 Hz, 2 H), 1.2–2.1 (m, 9 H), 0.03 (s, 9 H).

The alcohol obtained above (348 mg, 0.71 mmol) was dissolved immediately in 7 mL of acetonitrile containing DMAP (286 mg, 2.34 mmol). The solution was cooled to 0 °C, treated with *tert*-butyldimethylsilyl triflate (281.5 mg, 244 μL, 1.07 mmol), and slowly warmed to rt. After 2 h, the mixture was diluted with 20 mL of ether and washed with 10 mL of saturated aqueous sodium bicarbonate followed by 10 mL of saturated aqueous sodium chloride. The combined aqueous layers were washed with an additional 20 mL of ether, the combined organic layers were dried over magnesium sulfate and filtered, and the solvents were removed in vacuo. Flash chromatography (silica gel, 4:1 hexane–ether) yielded 26 mg of the partially purified alcohol and 338 mg

(78% based on recovered starting material, 66% for two steps) of the titled product as a clear colorless oil, a 1:1 mixture of diastereomers. IR ($CDCl_3$): 1740, 1630, 1460, 1440, 1420, 1350, 1140, 1080, 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.87 (dd, J = 7.3, 1.7 Hz, 2 H), 7.4–7.6 (m, 3 H), 6.93 (dd, J = 14.8, 3.3 Hz, 1 H), 6.46 (2 dd, J = 14.9, 1.6 Hz, 1 H), 5.45 (s, 0.5 H), 5.44 (s, 0.5 H), 4.95 (s, 0.5 H), 4.91 (s, 0.5 H), 4.88 (s, 1 H), 4.34 (m, 1 H), 3.77 (s, 1.5 H), 3.76 (s, 1.5 H), 3.00 (m, 2 H), 2.62 (m, 2 H), 1.7–2.1 (m, 8 H), 0.81 (s, 9 H), 0.02 (s, 9 H), 0.00 (s, 1.5 H), –0.01 (s, 1.5 H), –0.10 (s, 1.5 H), –0.12 (s, 1.5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 155.1, 148.8, 141.8, 140.6, 133.4, 130.1, 129.4, 127.7, 114.5, 114.4, 80.8, 70.7, 70.6, 55.8, 55.7, 54.7, 31.4, 31.3, 30.3, 30.0, 26.6, 26.3, 25.7, 25.6, 25.4, 23.7, 17.7, –1.6, –5.1, –5.2, –5.3. Mass: calcd for $C_{28}H_{46}O_3Si_2S_3$ $(M - CH_3OCO_2H)^+$ 582.2148, found 582.2117.

Preparation of (*E*)-1-(Phenylsulfonyl)-3-((*tert*-butyldimethylsilyl)oxy)-6-oxo-7-((methoxycarbonyl)oxy)-8-((trimethylsilyl)methyl)-1,8-nonadiene (8). Ketone 8 was prepared from dithiane 7 on a 0.51-mmol scale by the method described for 6. Flash chromatography (silica gel, 1:1 hexane–ether) gave 228 mg (79%) of the titled product as a clear viscous oil, a 1:1 mixture of diastereomers. IR ($CDCl_3$): 1750, 1730, 1630, 1460, 1440, 1080, 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.85 (ddd, J = 7.4, 1.8 Hz, 2 H), 7.61 (t, J = 7.0 Hz, 1 H), 7.53 (t, J = 7.3 Hz, 2 H), 6.88 (dd, J = 14.9, 4.1 Hz, 1 H), 6.47 (dd, J = 14.9, 1.6 Hz, 1 H), 5.15 (s, 0.5 H), 5.14 (s, 0.5 H), 5.06 (s, 0.5 H), 5.05 (s, 0.5 H), 4.90 (s, 1 H), 4.40 (m, 1 H), 3.78 (s, 3 H), 2.51 (m, 2 H), 1.6–2.0 (m, 2 H), 1.47 (s, 2 H), 0.80 (s, 9 H), 0.01 (s, 9 H), –0.02 (s, 1.5 H), –0.04 (s, 1.5 H), –0.12 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.1, 204.0, 155.1, 148.1, 148.0, 140.6, 139.8, (2), 133.5, 130.8, 130.7, 129.4, 127.7, 114.5, 114.4, 85.2, 85.1, 69.5, 55.0, 32.1, 32.0, 29.9, 25.4, 22.0, 17.8, –1.7, –5.2, –5.5. Mass: calcd for $C_{25}H_{41}O_5SSi_2$ $(M - CH_3OCO)^+$ 509.2213, found 509.2202. Anal. Calcd for $C_{27}H_{44}O_7SSi_2$: C, 56.99; H, 7.81. Found: C, 57.11; H, 7.62.

Preparation of 1,1-Bis(methylthio)-5,5-dimethoxypentane (10). A 1.40 M solution of *n*-butyllithium in hexane (15.9 mL, 22.3 mmol) was added via syringe to a stirred solution of bis(methylthio)methane (2.41 g, 2.28 mL, 22.3 mmol) in 30 mL of THF at –78 °C. The mixture was warmed to 0 °C over a period of 2.5 h and stirred at that temperature for an additional 45 min. At that point, the solution was recooled to –78 °C, bromoacetal 9 (4.0 g, 20.3 mmol) was slowly added via syringe, and the mixture warmed to rt over 16 h. The reaction mixture was then diluted with 150 mL of ether and washed with 50 mL of water. The organic layer was dried over magnesium sulfate, filtered, and concentrated in vacuo to yield 4.74 g (95%) of the titled product as a clear colorless liquid of sufficient purity to take directly to the next step. IR ($CDCl_3$): 1710, 1460, 1440, 1420 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.35 (t, J = 5.6 Hz, 1 H), 3.61 (t, J = 7.2 Hz, 1 H), 3.29 (s, 6 H), 2.06 (s, 6 H), 1.75 (q, J = 7.0 Hz, 2 H), 1.58 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 88.7, 53.8, 52.2, 33.9, 31.4, 22.2, 11.9. Mass: calcd for $C_8H_{16}OS_2$ $(M - CH_3OH)^+$ 192.0643, found 192.0644.

Preparation of 8,8-Dimethoxy-4,4-bis(methylthio)-3-acetoxy-2-((trimethylsilyl)methyl)-1-octane (11b). A 1.40 M solution of *n*-butyllithium in hexane (5.0 mL, 7.0 mmol) was added via syringe to a stirred solution of thioacetal 10 (1.68 g, 1.58 mL, 7.5 mmol) in 10 mL of THF at –78 °C. The mixture was warmed to 0 °C over a period of 1 h and stirred at that temperature for an additional 1.5 h. At that point, the bright yellow solution was recooled to –78 °C and aldehyde 1 (716 mg, 5.0 mmol) was slowly added via syringe. The solution was stirred at –78 °C for an additional 30 min and slowly warmed to –25 °C. At that temperature, the reaction mixture was poured into 30 mL of water and extracted with 30-mL portions of ether. The combined organic extracts were dried over sodium sulfate, filtered, and the solvents removed in vacuo. The residue was purified by flash chromatography (silica gel, 10:1 hexane–ether, 1% triethylamine) to give 1.2 g (65%) of alcohol 11a as a yellow oil, which was carried on without further purification. ^1H NMR (300 MHz, $CDCl_3$): δ 5.06 (s, 1 H), 4.88 (s, 1 H), 4.33 (t, J = 5.7 Hz, 1 H), 4.01 (d, J = 2.4 Hz, 1 H), 3.27 (2 s, 6 H), 2.91 (d, J = 2.4 Hz, 1 H), 2.06 (s, 6 H), 1.78 (d, J = 12.6 Hz, 1 H), 1.70 (d, J = 12.6 Hz, 1 H), 1.55 (m, 6 H), 0.02 (s, 9 H).

The above product (1.2 g, 3.25 mmol) in 7.7 mL of pyridine was treated with acetic anhydride (2.5 g, 2.3 mL, 25 mmol) and DMAP (43 mg, 0.35 mmol) overnight. After removal of the solvent in vacuo, the residue was purified via flash chromatography (silica gel, 10:1 hexane–ether, 1% triethylamine) to give 943 mg (46% overall) of the titled product as a clear colorless oil. IR ($CDCl_3$): 1740, 1630, 1440, 1420 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.35 (s, 1 H), 5.05 (s, 1 H), 4.91 (s, 1 H), 4.34 (t, J = 6.2 Hz, 1 H), 3.28 (s, 6 H), 2.09 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H), 1.4–2.7 (m, 8 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.4, 142.8, 114.2, 104.1, 79.1, 64.9, 52.4 (2), 35.2, 32.4, 24.7, 20.8, 19.9, 12.4, 12.3, –1.5. Mass: calcd for $C_{17}H_{33}O_4SSi$ $(M - CH_3S)^+$ 361.1869, found 361.1845.

Preparation of 4,4-Bis(methylthio)-3-acetoxy-2-((trimethylsilyl)methyl)-1-octen-8-al (12). The above acetal 11b (200 mg, 0.49 mmol) in 2.25 mL of THF was warmed with 0.75 mL of 1 N sulfuric acid at 40 °C for 4 h. The resulting solution was diluted with 12 mL of ether and washed with 2 mL of saturated aqueous sodium chloride. The aqueous layer was washed with two 2-mL portions of ether, and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated in vacuo to give 177 mg (100%) of the titled product as a clear colorless oil which was used without further purification. IR ($CDCl_3$): 2710, 1730, 1620, 1420, 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.75 (t, J = 1.5 Hz, 1 H), 5.34 (s, 1 H), 5.05 (s, 1 H), 4.90 (s, 1 H), 2.41 (td, J = 6.8, 1.5 Hz, 2 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.07 (s, 3 H), 1.6–2.0 (m, 6 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.1, 169.4, 142.8, 114.1, 78.7, 64.6, 43.6, 34.8, 24.9, 20.8, 17.5, 12.4, 12.2, –1.5. Mass: calcd for $C_{16}H_{30}O_3S_2Si$ (M^+) 362.1406, found 362.1391.

Preparation of (*E*)-1-(Phenylsulfonyl)-6,6-bis(methylthio)-7-acetoxy-8-((trimethylsilyl)methyl)-1,8-nonadiene (13). The titled compound was prepared from aldehyde 12 on a 0.47-mmol scale by the method described for 5. Flash chromatography (silica gel, 1:1 hexane–ether) gave 161 mg (70%) of the product as a clear viscous oil. IR ($CDCl_3$): 1730, 1630, 1440, 1420, 1140, 1080, 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (dd, J = 7.0, 1.7 Hz, 2 H), 7.58 (m, J = 7.3 Hz, 1 H), 7.52 (t, J = 7.3 Hz, 2 H), 6.94 (dt, J = 15.2, 6.8 Hz, 1 H), 6.32 (dt, J = 15.0, 1.5 Hz, 1 H), 5.31 (s, 1 H), 5.00 (s, 1 H), 4.87 (s, 1 H), 2.20 (q, J = 6.0 Hz, 2 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.01 (s, 3 H), 1.6–1.9 (m, 6 H), 0.01 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 146.3, 142.8, 140.7, 133.4, 131.0, 129.3, 127.6, 114.1, 78.7, 64.5, 34.7, 31.3, 24.9, 22.8, 20.8, 12.4, 12.3, –1.5.

Preparation of (*E*)-1-(Phenylsulfonyl)-6-oxo-7-acetoxy-8-((trimethylsilyl)methyl)-1,8-nonadiene (14). The titled compound was prepared from thioacetal 13 on a 0.30-mmol scale by the method described for 6. Flash chromatography (silica gel, 1:1 hexane–ether) gave 60 mg (47%) of the product as a clear colorless oil. IR ($CDCl_3$): 1740, 1720, 1630, 1440, 1140, 1080, 850 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ, 7.85 (dd, J = 7.0, 1.5 Hz, 2 H), 7.60 (m, J = 7.2 Hz, 1 H), 7.52 (t, J = 7.4 Hz, 2 H), 6.92 (dt, J = 15.1, 6.8 Hz, 1 H), 6.31 (dt, J = 15.1, 1.5 Hz, 1 H), 5.23 (s, 1 H), 5.04 (s, 1 H), 4.90 (s, 1 H), 2.47 (td, J = 6.9, 5.0 Hz, 2 H), 2.20 (q, J = 7.0 Hz, 2 H), 2.11 (s, 3 H), 1.72 (m, 2 H), 1.47 (s, 2 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.9, 170.3, 146.0, 140.7, 139.9, 133.4, 131.3, 129.4, 127.7, 114.8, 82.9, 36.1, 30.1, 22.0, 20.9, 20.4, –1.6. Mass: calcd for $C_{21}H_{30}O_5SSi$ (M^+) 422.1583, found 422.1630. Anal. Calcd for $C_{21}H_{30}O_5SSi$: C, 59.67; H, 7.17. Found: C, 59.39; H, 7.17.

Preparation of 2-(4,4-Dimethoxybutyl)-2-(2-((methoxycarbonyl)oxy)-3-((trimethylsilyl)methyl)-3-buten-2-yl)-1,3-dithiane (18). A 1.7 M solution of *tert*-butyllithium (5.86 mL, 9.97 mmol) in pentane was added via syringe to a solution of 2-bromo-3-(trimethylsilyl)propene[2,23] (1.05 g, 5.44 mmol) in 15 mL of ether at –78 °C. After 45 min at that temperature, 1 h at 0 °C, and recooling to –78 °C, the vinyllithium solution was transferred via cannula to a flask containing ketone 17[24] (1.26 g, 4.53 mmol) in 15 mL of ether at –78 °C. The resulting mixture was warmed to 0 °C, stirred for 1 h, warmed to rt, and treated with methyl chloroformate (1.42 g, 1.2 mL, 15 mmol). After 1.5 h, the cloudy suspension was poured into 200 mL of ether and

(23) Trost, B. M.; Coppola, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 6879.
(24) Prepared by alkylation of 2-acetyldithiane (ref 13) with 1,1-dimethoxy-4-iodobutane; Niwa, H.; Hasegawa, T.; Ban, N.; Yamada, K. *Tetrahedron* **1987**, *43*, 825.
(25) Moody, C. J.; Robert, S. M.; Toczek, J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1041.

washed with 100 mL of saturated aqueous sodium bicarbonate, and the aqueous layer washed with two 50-mL portions of ether. The combined organic layers were dried over magnesium sulfate, filtered, and concentrated in vacuo. Flash chromatography (silica gel, 10:1 hexane–ether) gave 1.26 g (62%) of the titled compound as a clear, colorless oil. IR ($CDCl_3$): 1749, 1625, 1440 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.06 (s, 1 H), 5.04 (s, 1 H), 5.04 (s, 1 H), 4.35 (t, J = 5.6 Hz, 1 H), 3.70 (s, 3 H), 3.29 (s, 3 H), 3.28 (s, 3 H), 3.20 (ddd, J = 13.1, 10.6, 5.0 Hz, 2 H), 2.60 (m, 2 H), 2.00 (m, 1 H), 1.91 (s, 3 H), 1.51–1.9 (m, 9 H), 0.07 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.1, 145.1, 114.9, 104.4, 95.7, 60.7, 53.7, 52.3, 52.1, 36.3, 32.8, 27.7, 27.2, 23.4, 23.1, 21.3, 20.7, –0.8. Mass: calcd for $C_{18}H_{35}O_2S_2Si$ (M – CH_3OCO_2) 375.1847, found 375.1837.

Preparation of 2-(4-Oxobutyl)-2-(2-((methoxycarbonyl)oxy)-3-((trimethylsilyl)methyl)-3-buten-2-yl)-1,3-dithiane (19). A solution of the above acetal **18** (1.25 g, 2.8 mmol) in 15 mL of THF was warmed with 4.5 mL of 1 N sulfuric acid to 40 °C. After 4 h, the mixture was diluted with 75 mL of ether and washed with 15 mL of saturated aqueous sodium chloride. The aqueous layer was extracted with two 15-mL portions of ether, and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated in vacuo to give 1.09 g (96%) of the titled product as a clear, colorless oil. IR ($CDCl_3$): 1750, 1720, 1630, 1480, 1420, 850 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.74 (t, J = 1.7 Hz, 1 H), 5.04 (s, 2 H), 3.70 (s, 3 H), 3.20 (m, 2 H), 2.64 (m, 2 H), 2.39 (td, J = 7.2, 1.8 Hz, 2 H), 1.9–2.2 (m, 3 H), 1.92 (s, 3 H), 1.6–1.9 (m, 5 H), 0.07 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.2, 153.0, 145.0, 114.9, 95.3, 60.7, 53.8, 43.9, 35.8, 27.7, 27.2, 23.4, 23.2, 21.3, 18.5, –0.8. Mass: calcd for $C_{17}H_{29}O_4S_2Si$ (M – CH_3)$^+$ 389.1276, found 389.1245.

Preparation of 2-((*E*)-5-(Phenylsulfonyl)-4-pentenyl)-2-(2-((methoxycarbonyl)oxy)-3-((trimethylsilyl)methyl)-3-buten-2-yl)-1,3-dithiane (20). The titled compound was prepared from the above alcohol **19** on a 2.70-mmol scale by the method described for **5**. Flash chromatography (silica gel, 3:1 hexane–ether) gave 1.19 g (81%) of **20** as a clear, colorless glass. IR ($CDCl_3$): 1750, 1620, 1440, 1150, 1090, 850 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (dd, J = 7.0, 1.6 Hz, 2 H), 7.60 (tm, J = 7.5 Hz, 1 H), 7.51 (tm, J = 7.5 Hz, 2 H), 6.97 (dt, J = 15.1, 7.1 Hz, 1 H), 6.33 (dm, J = 15.1, 1.6 Hz, 1 H), 4.99 (s, 1 H), 4.98 (s, 1 H), 3.69 (s, 3 H), 3.18 (m, 2 H), 2.58 (m, 2 H), 2.19 (q, J = 7.1 Hz, 2 H), 2.00 (m, 1 H), 1.7–2.0 (m, 3 H), 1.86 (s, 3 H), 1.5–1.8 (m, 2 H), 1.67 (d, J = 15.2 Hz, 1 H), 1.54 (d, J = 15.2 Hz, 1 H), 0.05 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7, 146.3, 144.7, 140.8, 132.9, 130.7, 128.9, 127.2, 114.6, 95.0, 60.2, 53.5, 35.3, 31.2, 27.4, 26.9, 23.2, 23.0, 22.9, 21.0, –1.0. Mass: calcd for $C_{23}H_{35}O_2S_3Si$ (M – CH_3OCO_2)$^+$ 467.1568, found 467.1566.

Preparation of (*E*)-1-(Phenylsulfonyl)-6-oxo-7-((methoxycarbonyl)oxy)-7-methyl-8-((trimethylsilyl)methyl)-1,8-nonadiene (21). The titled compound was prepared from dithiane **20** on a 2.03-mmol scale by the method described for **6**. Flash chromatography (silica gel, 4:1 hexane–ethyl acetate) gave 400 mg (44%) of ketone **21** as a clear, light yellow oil. IR ($CDCl_3$): 1746, 1722, 1630, 1444, 1148, 1087, 1076 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.85 (dd, J = 7.0, 1.6 Hz, 2 H), 7.56 (t, J = 7.2 Hz, 1 H), 7.52 (t, J = 7.4 Hz, 2 H), 6.92 (dt, J = 15.1, 7.1 Hz, 1 H), 6.30 (dt, J = 15.1, 1.5 Hz, 1 H), 5.00 (s, 1 H), 4.82 (s, 1 H), 3.76 (s, 3 H), 2.41 (m, J = 7.0 Hz, 2 H), 2.20 (q, J = 6.9 Hz, 2 H), 1.72 (p, J = 7.0 Hz, 2 H), 1.62 (s, 3 H), 1.55 (d, J = 14.6 Hz, 1 H), 1.40 (d, J = 14.6 Hz, 1 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.8, 154.5, 146.2, 144.6, 141.0, 133.3, 131.3, 129.3, 127.7, 111.3, 90.0, 54.7, 33.9, 30.2, 21.4, 20.6, 20.0, –1.3. Anal. Calcd for $C_{22}H_{32}O_6SSi$: C, 58.37; H, 7.14. Found: C, 58.16; H, 7.01.

Preparation of 1,1-Bis(methylthio)-6-((*tert*-butyldimethylsilyl)oxy)hexane (22, *n* = 3). A 1.52 M solution of *n*-butyllithium in hexane (10.3 mL, 15.6 mmol) was added via syringe to a stirred solution of bis(methylthio)methane (1.69 g, 1.60 mL, 1.56 mmol) in 20 mL of THF at –78 °C. After warming to 0 °C over a period of 2.5 h, stirring for 45 min, and recooling to –78 °C, 5-(*tert*-butyldimethylsiloxy)-1-bromopentane (4.0 g, 14.2 mmol) was slowly added via syringe, and the mixture warmed to rt over 16 h. The reaction mixture was then diluted with 150 mL of ether and washed with 50 mL of water. The organic layer was dried over magnesium sulfate, filtered, and concentrated in vacuo to yield 4.46 g (93%) of the titled compound as a clear colorless liquid of sufficient purity for further manipulation. IR ($CDCl_3$): 1471, 1437, 1424, 1389, 1361, 1257, 1095, 1006 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.61 (t, J = 7.2 Hz, 1 H), 3.58 (t, J = 6.4 Hz, 2 H), 2.07 (s, 6 H), 1.74 (q, J = 7.5 Hz, 2 H), 1.50 (m, J = 7.3 Hz, 4 H), 1.32 (m, J = 7.0 Hz, 2 H), 0.86 (s, 9 H), 0.02 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 62.9, 54.3, 34.4, 32.4, 27.1, 25.7, 25.1, 18.0, 12.2, –5.7. Mass: calcd for $C_{13}H_{29}OSSi$ (M – CH_3S)$^+$ 261.1709, found 261.1704.

Preparation of 1,1-Bis(methylthio)-4-((*tert*-butyldimethylsilyl)oxy)butane (22, *n* = 1). The titled compound was prepared on a 34.5-mmol scale from 3-*tert*-butyldimethylsiloxy)-1-bromopropane[26] described above for **22**, n = 3. Distillation, bp 105–109 °C (0.55 mmHg), yielded 6.41 g (74%) of thioacetal **22**, n = 1, as a yellow liquid. IR ($CDCl_3$): 1257, 1104 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.63 (t, J = 6.9 Hz, 1 H), 3.60 (t, J = 6.0 Hz, 2 H), 2.06 (s, 6 H), 1.80 (m, 4 H), 0.85 (s, 9 H), 0.01 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 62.4, 54.4, 31.1, 30.5, 25.7, 18.0, 12.3, –5.6. Mass: calcd for $C_{12}H_{28}OS_2Si$ (M^+) 280.1351, found 280.1345.

Preparation of 4,4-Bis(methylthio)-3-((methoxycarbonyl)oxy)-2-((trimethylsilyl)methyl)-1-nonen-9-ol (23, *n* = 3). A 1.40 M solution of *n*-butyllithium in hexane (3.0 mL, 4.1 mmol) was added via syringe to a stirred solution of the thioacetal **22** (n = 3) (1.33 g, 4.3 mmol) in 8 mL of THF at –78 °C. After warming to 0 °C over a period of 1.5 h and recooling to –78 °C, aldehyde **1** (508 mg, 3.6 mmol) was slowly added via syringe. The solution was stirred at –78 °C for an additional 30 min, slowly warmed to –25 °C, and treated with methyl chloroformate (709 mg, 583 μL, 7.5 mmol). After slowly warming to 0 °C, the mixture was stirred for 2 h, diluted with 25 mL of ether, and washed with 25 mL of saturated aqueous sodium bicarbonate. The aqueous layer was extracted with two 25-mL portions of ether, the combined organic extracts were dried over magnesium sulfate and filtered, and the solvents were removed in vacuo. The residue was dissolved in 24 mL of THF and treated with 6 mL of 1 N sulfuric acid for 2 h. At this point, the mixture was diluted with 120 mL of ether and washed with 20 mL of saturated aqueous sodium chloride. The aqueous layer was extracted with two 20-mL portions of ether, and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated in vacuo. Flash chromatography (silica gel, 3:1 hexane–ether, 1% acetic acid) gave 650 mg (46%) of the titled product as a yellow oil. IR ($CDCl_3$): 1747, 1625, 1443 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.20 (s, 1 H), 5.07 (s, 1 H), 4.93 (s, 1 H), 3.76 (s, 3 H), 3.62 (t, J = 6.5 Hz, 2 H), 2.10 (s, 3 H), 2.06 (s, 3 H), 1.89 (s, 2 H), 1.7–1.9 (m, 2 H), 1.55 (m, 5 H), 1.30 (m, 2 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.0, 142.3, 114.7, 83.7, 64.5, 63.5, 54.7, 35.3, 32.2, 25.8, 24.2, 12.5, –1.6. Mass: calcd for $C_{16}H_{31}O_4SSi$ (M – CH_3S)$^+$ 347.1712, found 347.1734.

Preparation of 4,4-Bis(methylthio)-3-((methoxycarbonyl)oxy)-2-((trimethylsilyl)methyl)-1-hepten-7-ol (23, *n* = 1). The titled compound was prepared from thioacetal **22** (n = 1) on a 15-mmol scale by the method described for **23** (n = 3). Flash chromatography (silica gel, 3:1 hexane–ethyl acetate) gave 2.44 g (44%) of the product **23** (n = 1) as a yellow, viscous oil. IR ($CDCl_3$): 3627, 1746, 1645, 1443 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.20 (s, 1 H), 5.09 (s, 1 H), 4.94 (s, 1 H), 3.76 (s, 3 H), 3.61 (m, 2 H), 2.11 (s, 3 H), 2.08 (s, 3 H), 1.87 (m, 7 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9, 142.1, 114.6, 83.5, 64.1, 62.2, 54.5, 31.5, 27.7, 24.2, 12.3, 12.2, –1.7. Mass: calcd for $C_{15}H_{30}O_4S_2Si$ (M^+) 366.1354, found 366.1385.

Preparation of 4,4-Bis(methylthio)-3-((methoxycarbonyl)oxy)-2-((trimethylsilyl)methyl)-1-nonen-9-al (24, *n* = 3). To a stirred suspension of the above alcohol **23** (n = 3) (1.13 g, 2.87 mmol) and Celite (1.4 g) in 7.5 mL of methylene chloride was added PCC (841 mg, 3.9 mmol) at rt. After 3 h, the orange suspension had become dark brown and was then diluted with 10 mL of ether and treated with anhydrous sodium sulfate. After 10 min, the slurry was filtered through a short pad of silica gel, eluting first with hexane and then ether, dried over magnesium sulfate, and refiltered. Removal of the solvent in vacuo gave 876 mg (78%) of the titled product as a clear, colorless oil. IR ($CDCl_3$): 1747, 1724, 1630, 1443, 1422 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$):

(26) Wilson, S. R.; Zucker, P. A. *J. Org. Chem.* **1988**, *53*, 4682.

δ 9.75 (t, J = 1.5 Hz, 1 H), 5.18 (s, 1 H), 5.07 (s, 1 H), 4.93 (s, 1 H), 3.76 (s, 3 H), 2.42 (m, 2 H), 2.10 (s, 3 H), 2.06 (s, 3 H), 1.85 (s, 2 H), 1.75 (m, 2 H), 1.59 (m, 4 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.4, 154.9, 142.3, 114.6, 83.4, 64.3, 54.7, 43.4, 35.1, 24.3, 24.1, 21.9, 12.4, -1.7. Mass: calcd for $C_{16}H_{29}O_4SSi$ (M - CH_3S)$^+$ 345.1556, found 345.1547.

Preparation of 4,4-Bis(methylthio)-3-((methoxycarbonyl)oxy)-2-((trimethylsilyl)methyl)-1-hepten-7-al (24, *n* = 1). The titled compound was prepared from thioacetal **23** (*n* = 1) on a 4.1-mmol scale by the method described for **24** (*n* = 3). Flash chromatography (silica gel, 10:1 hexane–ether) gave 950 mg (64%) of the product **24** (*n* = 1) as a clear, colorless oil. IR ($CDCl_3$): 1747, 1723, 1630, 1443 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.79 (s, 1 H), 5.15 (s, 1 H), 5.06 (s, 1 H), 4.94 (s, 1 H), 3.77 (s, 3 H), 2.83 (tm, J = 7.9 Hz, 2 H), 2.14 (m, 2 H), 2.09 (s, 3 H), 2.06 (s, 3 H), 1.86 (s, 2 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.9, 154.9, 142.4, 114.8, 83.5, 63.8, 54.7, 39.8, 27.1, 24.6, 12.5, 12.3, -1.6. Mass: Calcd for $C_{15}H_{28}O_4S_2Si$ (M^+) 364.1199, found 364.1166.

Preparation of (*E*)-1-(Phenylsulfonyl)-7,7-bis(methylthio)-8-((methoxycarbonyl)oxy)-9-((trimethylsilyl)methyl)-1,9-decadiene (25, *n* = 3). The titled compound was prepared from the aldehyde **24** (*n* = 3) on a 2.18-mmol scale by the method described for **5**. Flash chromatography (silica gel, 1:1 hexane–ether) gave 955 mg (81%) of the product **25** (*n* = 3) as a clear viscous oil. IR ($CDCl_3$): 1747, 1628, 1443, 1422, 1148, 1087 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (dd, J = 7.0, 1.6 Hz, 2 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.51 (t, J = 6.9 Hz, 2 H), 6.97 (dt, J = 15.1, 7.1 Hz, 1 H), 6.30 (d, J = 15.1 Hz, 1 H), 5.16 (s, 1 H), 5.02 (s, 1 H), 4.91 (s, 1 H), 3.75 (s, 3 H), 2.23 (q, J = 6.9 Hz, 2 H), 2.07 (s, 3 H), 2.03 (s, 3 H), 1.83 (s, 2 H), 1.75 (m, 2 H), 1.55 (m, 2 H), 1.40 (m, 2 H), 0.01 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.0, 146.8, 142.3, 140.9, 133.3, 130.7, 129.4, 127.7, 114.6, 83.5, 64.4, 54.7, 35.1, 31.0, 27.7, 24.4, 24.1, 12.5, -1.6. Mass: Calcd for $C_{23}H_{35}O_5S_2Si$ (M - CH_3S)$^+$ 483.1695, found 483.1680.

Preparation of (*E*)-1-(Phenylsulfonyl)-5,5-bis(methylthio)-6-((methoxycarbonyl)oxy)-7-((trimethylsilyl)methyl)-1,7-octadiene (25, *n* = 1). The titled compound was prepared from the aldehyde **24** (*n* = 1) on a 1.18-mmol scale by the method described for **5**. Flash chromatography (silica gel, solvent gradient, 3:1 to 1:1 hexane–ether) gave 471 mg (85%) of the product **25** (*n* = 1) as a clear, colorless oil. IR ($CDCl_3$): 1748, 1629, 1443, 1148, 1087 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (dd, J = 7.3, 1.6 Hz, 2 H), 7.61 (t, J = 7.2 Hz, 1 H), 7.52 (t, J = 7.5 Hz, 2 H), 6.94 (dt, J = 15.1, 6.9 Hz, 1 H), 6.31 (d, J = 15.1, 1 H), 5.14 (s, 1 H), 5.03 (s, 1 H), 4.92 (s, 1 H), 3.24 (s, 3 H), 2.54 (q, J = 7.2 Hz, 2 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 1.7–2.1 (m, 4 H), 0.01 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.6, 145.8, 142.0, 140.7, 133.1, 130.8, 129.1, 127.4, 114.5, 82.9, 63.7, 54.5, 32.8, 26.9, 24.4, 12.2, 12.0, -1.8. Mass: calcd for $C_{21}H_{31}O_5S_2Si$ (M - CH_3S)$^+$ 455.1382, found 455.1371.

Preparation of (*E*)-1-(Phenylsulfonyl)-7-oxo-8-((methoxycarbonyl)oxy)-9-((trimethylsilyl)methyl)-1,9-decadiene (26, *n* = 3). The titled compound was prepared from thioacetal **25** (*n* = 3) on a 1.42-mmol scale by the method described for **6**. Flash chromatography (silica gel, 2:1 hexane–ether) gave 398 mg (62%) of the product **26** (*n* = 3) as a clear, light yellow oil. IR ($CDCl_3$): 1750, 1731, 1634, 1445, 1148, 1087, cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (dd, J = 7.1, 1.6 Hz, 2 H), 7.57 (tm, J = 7.2 Hz, 1 H), 7.52 (t, J = 7.2 Hz, 2 H), 6.95 (dt, J = 15.2, 6.8 Hz, 1 H), 6.29 (dt, J = 15.0, 1.6 Hz, 1 H), 5.16 (s, 1 H), 5.09 (s, 1 H), 4.92 (s, 1 H), 3.78 (s, 3 H), 2.48 (td, J = 7.0, 3.8 Hz, 2 H), 2.21 (q, J = 6.6 Hz, 2 H), 1.3–1.6 (m, 4 H), 1.48 (s, 2 H), 0.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.0, 154.9, 146.5, 140.6, 139.6, 133.2, 130.6, 129.2, 127.4, 114.3, 85.0, 54.8, 36.5, 30.7, 26.4, 22.1, 21.8, -1.9. Mass: calcd for $C_{22}H_{32}O_6SSi$ (M^+) 452.1688, found 452.1719. Anal. Calcd for $C_{22}H_{32}O_6SSi$: C, 58.37; H, 7.14. Found: C, 58.01; H, 6.89.

Preparation of (*E*)-1-(Phenylsulfonyl)-5-oxo-6-((methoxycarbonyl)oxy)-7-((trimethylsilyl)methyl)-1,7-octadiene (26, *n* = 1). Thioacetal **25** (*n* = 1) (178 mg, 0.35 mmol) in 1.5 mL of acetonitrile was added to a stirred slurry of NCS (186 mg, 1.4 mmol) and silver nitrate (241 mg, 1.53 mmol) in 6 mL of acetonitrile containing 1.5 mL of water at 0 °C. A voluminous precipitate formed, and the reaction was complete within 20 min. The mixture was treated successively with 4 mL of saturated aqueous sodium bicarbonate and 4 mL of saturated aqueous sodium chloride and poured into 50 mL of 1:1 hexane–methylene chloride. The biphasic mixture was filtered through Celite, rinsing the filtercake with 1:1 hexane–methylene chloride, and the layers were separated. The aqueous layer was washed with 15 mL of 1:1 hexane–methylene chloride, the combined organic layers were dried over magnesium sulfate and filtered, and the solvent was removed in vacuo. Flash chromatography (silica gel, 6:1 hexane–ethyl acetate) yielded 120 mg (81%) of the titled product as a clear, colorless oil. IR ($CDCl_3$): 1751, 1733, 1634, 1445, 1149, 1087 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (dd, J = 7.1, 1.5 Hz, 2 H), 7.60 (t, J = 7.3 Hz, 1 H), 7.51 (t, J = 7.4 Hz, 2 H), 6.91 (dt, J = 15.1, 6.6 Hz, 1 H), 6.30 (d, J = 15.1 Hz, 1 H), 5.15 (s, 1 H), 5.09 (s, 1 H), 4.91 (s, 1 H), 3.77 (s, 3 H), 2.67 (t, J = 7.5 Hz, 1 H), 2.66 (t, J = 6.7 Hz, 1 H), 2.49 (q, J = 6.8 Hz, 2 H), 1.45 (d, J = 15.3 Hz, 1 H), 1.38 (d, J = 15.3 Hz, 1 H), 0.01 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 202.5, 155.1, 144.8, 141.0, 139.9, 133.5, 131.8, 129.4, 127.9, 114.2, 85.1, 55.1, 34.9, 24.7, 22.2, -1.7. Mass: calcd for $C_{18}H_{25}O_4SSi$ (M - CH_3O_2C)$^+$ 365.1243, found 365.1267. Anal. Calcd for $C_{20}H_{28}O_6SSi$: C, 56.57; H, 6.66. Found: C, 56.54; H, 6.34.

Preparation of Standard Catalyst Solution. A standard catalyst solution was prepared on a scale 1–5 times that required for the reaction. Palladium acetate was dissolved in the appropriate solvent (THF or dioxane) to a concentration of 5 × 10^{-3} M. Six equivalents of triisopropyl phosphite were then added via syringe, and the mixture stirred for 10 min. An aliquot of this solution was then added via syringe to the substrate, such that the substrate concentration was 0.1 M. The reaction mixture thus produced contained 5 mol % palladium acetate and 30 mol % triisopropyl phosphite relative to the substrate.

Preparation of (6*R,7*R**)-9-Methyl-7-(phenylsulfonyl)-2-oxobicyclo[4.3.0]non-1-ene (27). Cycloaddition of 6.** A 1.5-mL aliquot (75%) of a solution of palladium(II) acetate (5.1 mg, 0.023 mmol) and triisopropyl phosphite (28.9 mg, 34.3 μL, 0.14 mmol) in 2 mL of THF was added to a solution of substrate **6** (152 mg, 0.35 mmol) in 2 mL of THF. After 5 h at rt, the solvent was removed under a stream of compressed air, and the crude product was allowed to crystallize from ether overnight, providing 51.4 mg of the titled product as fine, light yellow needles. The solvent was removed from the filtrate in vacuo, and 29.8 mg of additional product was isolated via flash chromatography (silica gel, 3:1 hexane–ethyl acetate) for an overall yield of 81.2 mg (81%), mp 147–148 °C (hexane–ethyl acetate). IR ($CDCl_3$): 1680, 1620, 1440, 1430, 1140, 1080 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (dd, J = 7.1, 1.4 Hz, 2 H), 7.67 (tt, J = 7.4, 1.5 Hz, 1 H), 7.58 (td, J = 7.0, 1.5 Hz, 2 H), 3.53 (q, J = 9.2 Hz, 1 H), 3.39 (m, 1 H), 2.95 (dddd, J = 17.3, 10.1, 2.3, 1.5 Hz, 1 H), 2.44 (ddm, J = 17.4, 9.0 Hz, 2 H), 2.16 (ddd, J = 17.5, 13.0, 6.3 Hz, 1 H), 1.99 (d, J = 1.1 Hz, 3 H), 1.96 (m, 2 H), 1.70 (qm, J = 13.7 Hz, 1 H), 1.28 (qd, J = 12.5, 3.3 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 147.7, 138.4, 133.9, 133.2, 129.4, 128.3, 68.4, 47.1, 40.7, 39.4, 31.4, 23.4, 15.6. Mass: calcd for $C_{10}H_{12}O$ (M - $C_6H_5SO_2H$)$^+$ 148.0888, found 148.0890. Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.17; H, 6.26. Found: C, 66.45; H, 6.41.

Cycloaddition of 14. Substrate **14** (12.9 mg, 0.031 mmol) was treated with a 310-μL aliquot of the catalyst solution prepared above in dioxane and the mixture heated at 100–120 °C for 1 h. After concentration in vacuo, the residue was purified via flash chromatography (silica gel, 3:1 hexane–ethyl acetate) to yield 6.8 mg (75%) of the titled product.

Cycloaddition of 8: Preparation of (1*S,5*R**,6*R**,7*R**)-9-Methano-7-(phenylsulfonyl)-5-((*tert*-butyldimethylsilyl)oxy)-2-oxobicyclo[4.3.0]nonane (28), (1*R**,5*S**,6*R**,7*R**)-9-Methano-7-(phenylsulfonyl)-5-((*tert*-butyldimethylsilyl)oxy)-2-oxobiyclo[4.3.0]nonane (29), (5*R**,6*R**,7*R**)-9-Methyl-7-(phenylsulfonyl)-5-((*tert*-butyldimethylsilyl)oxy)-2-oxobicyclo[4.3.0]non-1-ene (30), and (5*S**,6*R**,7*R**)-9-Methyl-7-(phenylsulfonyl)-5-((*tert*-butyldimethylsilyl)oxy)-2-oxobicyclo[4.3.0]non-1-ene (31).** Substrate **8** (142.6 mg, 0.251 mmol) was treated with a 2.5-mL aliquot of the catalyst solution prepared above in THF. After 9 h at rt, the solvent was removed in vacuo to give 111.7 mg of crude product as a 2.1:7.9:2.5:1.0 mixture of **28:29:30:31** (^{1}H NMR ratio of intensities of peaks at δ 0.80, 0.92, 0.89, and 0.82, respectively). Flash chromatography yielded 15.1 mg of **28**, 15.1

mg of **31**, and 65.0 mg of a 3.2:1.1 mixture of **29**:**30** (95.2 mg, 90% overall). **28** (white powder, mp 137–138 °C, hexane–ether). IR ($CDCl_3$): 1720, 1602, 1448, 1149, 1087 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, J = 7.2, 1.3 Hz, 2 H), 7.66 (tm, J = 7.5 Hz, 1 H), 7.56 (t, J = 7.6 Hz, 2 H), 5.48 (d, J = 2.4 Hz, 1 H), 5.05 (d, J = 2.1 Hz, 1 H), 4.74 (d, J = 1.5 Hz, 1 H), 3.58 (d, J = 13.6 Hz, 1 H), 3.50 (q, J = 9.8 Hz, 1 H), 2.55 (m, 3 H), 2.36 (dd, J = 17.0, 8.9 Hz, 1 H), 2.27 (ddd, J = 14.2, 5.0, 1.9 Hz, 1 H), 2.08 (ddt, J = 14.0, 6.9, 2.1 Hz, 1 H), 1.87 (tdd, J = 14.0, 5.1, 2.2 Hz, 1 H), 0.93 (s, 9 H), 0.26 (s, 3 H), 0.18 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.4, 139.1, 138.7, 134.1, 129.6, 128.6, 111.8, 65.7, 60.8, 51.6, 50.4, 37.2, 34.3, 34.0, 25.7, 17.9, −4.9, −5.0. Mass: calcd for $C_{22}H_{32}O_4SSi$ (M^+) 420.1790, found 420.1788. **31** (viscous oil). IR ($CDCl_3$): 1689, 1637, 1635, 1423, 1150, 1088 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, J = 7.4, 1.4 Hz, 2 H), 7.63 (t, J = 7.4 Hz, 1 H), 7.54 (t, J = 7.8 Hz, 2 H), 3.76 (td, J = 8.6, 4.2 Hz, 1 H), 3.65 (dt, J = 9.9, 5.0 Hz, 1 H), 3.51 (m, 1 H), 2.91 (dd, J = 19.1, 5.4 Hz, 1 H), 2.55 (m, 2 H), 2.25 (ddd, J = 17.7, 10.4, 6.4 Hz, 1 H), 2.01 (dq, J = 13.7, 5.4 Hz, 1 H), 1.88 (s, 3 H), 1.88 (m, 1 H), 0.89 (s, 9 H), 0.10 (s, 3 H), 0.07 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.9, 148.2, 138.3, 134.0, 132.8, 129.5, 129.0, 72.3, 64.2, 54.8, 40.1, 37.7, 32.0, 25.7, 17.8, 14.9, −4.7. Mass: calcd for $C_{18}H_{24}O_4SSi$ ($M - C_4H_8$)$^+$ 364.1165, found 364.1164; calcd for $C_{18}H_{23}O_4SSi$ ($M - C_4H_9$)$^+$ 363.1086, found 363.1107. **29** (viscous oil). ^1H NMR (300 MHz, $CDCl_3$): δ 7.85 (m, 2 H), 7.5–7.9 (m, 3 H), 5.02 (dd, J = 4.9, 1.2 Hz, 1 H), 4.85 (dd, J = 4.6, 1.5 Hz, 1 H), 3.71 (td, J = 8.2, 3.7 Hz, 1 H), 3.63 (bd, J = 8.0 Hz, 1 H), 3.47 (dt, J = 7.9, 4.6 Hz, 1 H), 2.95 (dm, J = 18.4 Hz, 1 H), 2.86 (td, J = 8.2, 4.9 Hz, 1 H), 2.64 (ddm, J = 18.4, 8.0 Hz, 1 H), 1.7–2.0 (m, 2 H), 0.80 (s, 9 H), 0.02 (s, 6 H).

Preparation of (5*R,6*R**,7*R**)-9-Methyl-7-(phenylsulfonyl)-5-hydroxy-2-oxobicyclo[4.3.0]non-1-ene (32).** The above 3:1 mixture of **29** and **30** (54.3 mg, 0.129 mmol) and 1.0 mL of a 1 M solution of tetra-*n*-butylammonium fluoride in THF was stirred at rt for 30 min, becoming dark purple during this time. The mixture was then diluted with 20 mL of ether and washed with 10 mL of water, and the aqueous layer extracted with two 5-mL portions of ether. The combined organic layers were dried over magnesium sulfate and filtered, and the solvent was removed in vacuo. Flash chromatography yielded 10.9 mg (28%, ~100% based on 3:1 ratio of starting material) of the titled product, a yellow oil, as the only isolable product. IR ($CDCl_3$): 3630, 3500, 1684, 1629, 1149, 1087, 1074 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, J = 7.1, 1.5 Hz, 2 H), 7.67 (tt, J = 7.4, 1.6 Hz, 1 H), 7.58 (t, J = 7.6 Hz, 2 H), 4.15 (bs, 1 H), 4.11 (q, J = 9.1 Hz, 1 H), 3.61 (dp, J = 8.8, 2.7 Hz, 1 H), 2.88 (dddd, J = 17.7, 9.5, 2.7, 1.5 Hz, 1 H), 2.56 (ddd, J = 17.7, 13.0, 6.8 Hz, 1 H), 2.39 (ddm, J = 17.7, 9.7 Hz, 1 H), 2.33 (ddd, J = 17.7, 5.6, 2.2 Hz, 1 H), 2.07 (dddd, J = 14.4, 6.7, 4.0, 2.5 Hz, 1 H), 2.01 (d, J = 1.3 Hz, 3 H), 1.94 (m, 1 H), 1.82 (bs, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.5, 150.4, 138.8, 134.2, 129.8, 129.6, 128.5, 65.5, 62.4, 51.3, 39.5, 34.6, 30.6, 15.7. Mass: calcd for $C_{10}H_{13}O_2$ ($M - C_6H_5SO_2$)$^+$ 165.0915, found 165.0903.

Cycloaddition of 21: Preparation of (6*R,7*R**)-9-Methylene-7-(phenylsulfonyl)-1-methyl-2-oxobicyclo[4.3.0]nonanes (35 and 36).** Substrate **21** (53.2 mg, 0.118 mmol) was treated with a 1.2-mL aliquot of the catalyst solution prepared above in dioxane, and the mixture was heated at 100 °C for 40 min, at which time the bright yellow solution became colorless. The solvent was removed in vacuo, and the residue was purified via flash chromatography (silica gel, 2:1 hexane–ether) to give 23.7 mg (66%) of cycloadducts as 2.4:1 mixture of isomers as indicated by the relative integration of ^1H NMR signals at δ 1.14 and 1.35, respectively. IR ($CDCl_3$): 1712, 1610, 1448, 1149, 1087 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.87 (dd, J = 7.1, 1.2 Hz, 2 H), 7.66 (m, 1 H), 7.56 (t, J = 7.6 Hz, 2 H), 5.49 (t, J = 2.4 Hz, 1 H), 4.96 (t, J = 2.0 Hz, 1 H), 3.40 (m, 1 H), 2.4–2.6 (m, 3 H), 2.3 (m, 3 H), 2.0 (m, 2 H), 1.7 (m, 1 H), 1.4 (s, 3 H). Minor isomer, partial: δ 5.01 (t, J = 2.0 Hz, 1 H), 4.86 (t, J = 2.2 Hz, 1 H), 3.37 (m, 1 H), 2.70 (m, 1 H), 1.35 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) major isomer: δ 209.7, 145.4, 138.9, 134.0, 129.5, 128.6, 110.6, 62.8, 55.7, 48.0, 37.5, 32.9, 24.5, 22.5, 20.4. Minor isomer, partial: δ 133.9, 110.0, 63.5, 49.2, 37.9, 33.4, 24.4, 22.4, 21.6. Mass: calcd for $C_{17}H_{20}O_3S$ (M^+) 304.1133, found 304.1168; calcd for $C_{11}H_{14}O$ ($M - C_6H_5SO_2$)$^+$ 163.1123. Found 163.1141.

Cycloaddition of 26 (*n* = 1): Preparation of (1*S,5*R**,6*R**)-8-Methylene-6-(phenylsulfonyl)-2-oxobicyclo[3.3.0]octane (37), (5*R**,6*R**)-8-Methyl-6-(phenylsulfonyl)-2-oxobicyclo[3.3.0]oct-1-ene (38), and (5*R**,6*S**)-8-Methyl-6-(phenylsulfonyl)-2-oxobicyclo[3.3.0]oct-1-ene (39).** Substrate **26** (n = 1) (86.8 mg, 0.20 mmol) was treated with a 2.0-mL aliquot of the catalyst solution prepared above, and the mixture was heated at 100 °C for 1.5 h. After evaporation in vacuo, flash chromatography (silica gel, 3:1 hexane–ethyl acetate) yielded 22.7 mg of a 3.1:1 mixture of **37** and **38**, as indicated by the relative integration of ^1H NMR resonances at δ 2.86 and 2.74, respectively, and 3.2 mg of **39** (25.9 mg, 47% overall). Exhaustive chromatography (silica gel, 3:1 hexane–ether) of the mixed products allowed the isolation of an analytical sample of **37**. Product **38** was isolated by treating a solution of **37** and **38** in 2 mL of THF with benzyltrimethylammonium methoxide (22.4 mg, 1.5 equiv. 0.123 mmol). After 30 min, the mixture was diluted with 5 mL of ether and washed with 2 mL of saturated aqueous ammonium chloride, and the aqueous layer was extracted with two 5-mL portions of ether. The organic extracts were dried over magnesium sulfate and filtered, and the solvent was removed in vacuo. The residue was purified via flash chromatography (silica gel, 3:1 hexane–ether) to give 10.2 mg (45%) of product **38**. **37** (colorless oil). IR ($CDCl_3$): 1742, 1610, 1448, 1410, 1149, 1087 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.4 Hz, 2 H), 7.68 (t, J = 7.6 Hz, 1 H), 7.58 (t, J = 7.7 Hz, 2 H), 5.18 (d, J = 2.1 Hz, 1 H), 5.01 (d, J = 1.8 Hz, 1 H), 3.37 (m, 2 H), 3.16 (d, J = 7.9 Hz, 1 H), 2.86 (dd, J = 16.7, 6.7 Hz, 1 H), 2.62 (dd, J = 16.7, 7.3 Hz, 1 H), 2.1–2.4 (m, 3 H), 1.76 (dt, J = 12.2, 5.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 134.0, 129.4, 128.6, 127.9, 110.7, 67.7, 55.9, 42.6, 36.6, 34.9, 25.7. Mass: calcd for $C_{15}H_{16}SO_3$ (M^+) 276.0820, found 276.0832. **38** (white crystalline) solid, mp 146–147 °C, $CDCl_3$). IR ($CDCl_3$): 1709, 1659, 1448, 1434, 1150, 1088 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, J = 7.1, 1.6 Hz, 2 H), 7.67 (m, 1 H), 7.58 (t, J = 7.1 Hz, 2 H), 3.69 (m, 1 H), 3.63 (dt, J = 9.8, 8.2 Hz, 1 H), 3.42 (ddm, J = 17.3, 9.8 Hz, 1 H), 2.79 (ddd, J = 17.3, 8.2, 1.2 Hz, 1 H), 2.43 (d, J = 14.6 Hz, 1 H), 2.41 (d, J = 14.6 Hz, 1 H), 2.00 (s, 3 H), 1.84 (m, 1 H), 1.36 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7, 145.8, 138.7, 138.0, 134.0, 129.5, 128.3, 70.8, 49.2, 43.8, 43.7, 28.6, 14.9. Mass: calcd for $C_9H_{11}O$ ($M - C_6H_5SO_2$)$^+$ 135.0810, found 135.0802. **39** (off-white solid, mp 131–132 °C, ether). IR ($CDCl_3$): 1712, 1666, 1448, 1429, 1409, 1149, 1087 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 7.3 Hz, 2 H), 7.67 (t, J = 7.3 Hz, 1 H), 7.57 (t, J = 7.3 Hz, 2 H), 3.96 (dt, J = 9.0, 6.0 Hz, 1 H), 3.73 (m, 1 H), 3.00 (d, J = 6.0 Hz, 2 H), 2.4–2.7 (m, 3 H), 2.22 (td, J = 7.5, 6.0 Hz, 1 H), 2.00 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.0, 144.8, 139.3, 139.2, 133.8, 129.4, 128.2, 62.1, 50.7, 44.9, 43.7, 24.9, 14.6. Mass: Calcd for $C_{15}H_{16}O_3S$ (M^+) 276.0820, found 276.0813.

Cycloaddition of 26 (*n* = 3): Preparation of (7*R,8*R**)-10-Methyl-8-(phenylsulfonyl)-2-oxobicyclo[5.3.0]dec-1-ene (40).** Substrate **26** (n = 3) (72.6 mg, 0.161 mmol) in 4.3 mL of dioxane was treated with a 3.2-mL aliquot of the catalyst solution prepared above in dioxane, and the mixture was heated at 100 °C for 2 h. After removal of solvent in vacuo, the residue was purified via flash chromatography (silica gel, 4:1 hexane–ethyl acetate) to give 24.9 mg (51%) of an 8.2:1 mixture of **40** and **41**, as indicated by the relative integration of ^1H NMR resonances at δ 3.51 and 5.07, respectively. Rechromatography allowed isolation of 23.0 mg (47%) of **40** as a colorless oil, which crystallized to a white powder, mp 120–121 °C ($CDCl_3$), upon extended storage. IR ($CDCl_3$): 1676, 1616, 1448, 1150, 1087, 1018 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (dd, J = 6.9, 1.6 Hz, 2 H), 7.66 (tm, J = 7.4 Hz, 1 H), 7.57 (t, J = 7.5 Hz, 2 H), 3.51 (m, 1 H), 3.31 (dt, J = 9.5, 6.9 Hz, 1 H), 2.91 (ddt, J = 19.0, 7.2, 1.4 Hz, 1 H), 2.59 (dd, J = 18.8, 9.4 Hz, 1 H), 2.47 (m, 2 H), 1.99 (d, J = 1.4 Hz, 3 H), 1.7–1.9 (m, 2 H), 1.2–1.6 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.5, 151.2, 138.6, 137.2, 134.2, 129.6, 128.7, 67.4, 47.9, 45.3, 39.8, 37.4, 30.0, 24.9, 16.1. Mass: calcd for $C_{17}H_{20}O_3S$ (M^+) 304.1133, found 304.1175; calcd for $C_{11}H_{15}O$ ($M - C_6H_5SO_2$)$^+$ 163.1122, found 163.1123.

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Registry No. 1, 56407-82-0; **2a**, 57795-10-5; **2b**, 115843-67-9; **3**, 137871-60-4; **4**, 137871-61-5; **5**, 137871-62-6; **6**, 137871-63-7; (*R**,*R**)-**7**, 137871-64-8; (*R**,*R**)-**7** alcohol, 137871-70-6; (*R**,*S**)-**7**, 137871-77-3; (*R**,*S**)-**7** alcohol, 137871-76-2; (*R**,*R**)-**8**, 137871-65-9; (*R**,*S**)-**8**, 137871-78-4; **9**, 24157-02-6; **10**, 137871-66-0; **11a**, 137871-92-2; **11b**, 137871-91-1; **12**, 137871-67-1; **13**, 137871-68-2; **14**, 137871-69-3; **15**, 137871-93-3; **16**, 137871-94-4; **17**, 137871-71-7; **18**, 137871-72-8; **19**, 137871-73-9; **20**, 137871-74-0; **21**, 137871-75-1; **22** (*n* = 1), 137871-96-6; **22** (*n* = 3), 137871-95-5; **23** (*n* = 1), 137871-97-7; **23** (*n* = 3), 137871-97-7; **24** (*n* = 1), 137872-00-5; **24** (*n* = 3), 137871-99-9; **25** (*n* = 1), 137872-02-7; **25** (*n* = 3), 137872-01-6; **26** (*n* = 1), 137872-04-9; **26** (*n* = 3), 137872-03-8; **27**, 137871-79-5; **28**, 137871-80-8; **29**, 137871-81-9; **30**, 137871-82-0; **31**, 137871-83-1; **32**, 137871-84-2; **35**, 137871-85-3; **36**, 137871-86-4; **37**, 137871-87-5; **38**, 137871-88-6; **39**, 137871-89-7; **40**, 137871-90-0; diethyl (phenylsulfonyl)methane phosphonate, 56069-39-7; [(4-chlorophenyl)sulfinyl]methyl phenyl sulfone, 133445-41-7; *tert*-butyldimethylsilyl triflate, 69739-34-0; bis(methylthio)methane, 1618-26-4; tetrahydrofuran, 109-99-9; 2-methyltetrahydropyran, 10141-72-7; 1,3-propanedithiol, 109-80-8; 2-bromo-3-(trimethylsilyl)propene, 81790-10-5; 2-acetyl-1,3-dithiane, 58277-26-2; 4-iodobutanal dimethyl acetal, 91988-32-8; 5-(*tert*-butyldimethylsiloxy)-1-bromopentane, 85514-43-8; 3-(*tert*-butyldimethylsiloxy)-1-bromopropane, 89031-84-5; palladium acetate, 3375-31-3; triisopropyl phosphite, 116-17-6; trimethylenemethane, 13001-05-3.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for all compounds lacking a combustion analysis and experimental procedures for **2a**, **2b**, **9**, **15**, **16**, 2-acetyl-1,3-dithiane, 4,4-dimethoxy-1-iodobutane, **17**, 3-(*tert*-butyldimethylsiloxy)-1-bromopropane, and 5-(*tert*-butyldimethylsiloxy)-1-bromopentane (33 pages). Ordering information is given on any current masthead page.

Sulfonylation of Organometallic Reagents with Arenesulfonyl Fluorides: A Simple One-Step Synthesis of Sulfones

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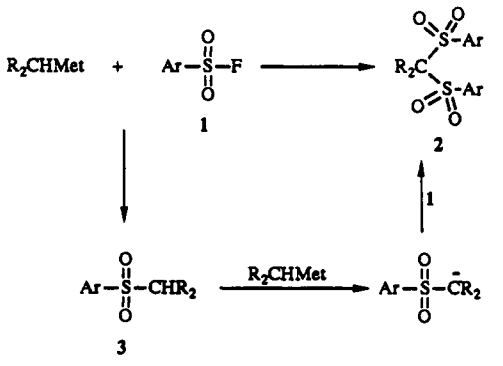
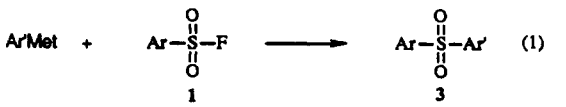
Sulfonylation of organometallic reagents was accomplished with arenesulfonyl fluorides to provide a wide variety of alkylaryl- and diaryl sulfones. Organolithium and diorganocopper lithium reagents react smoothly with arenesulfonyl fluorides to give sulfones in high yields. Alkyl Grignard reagents often lead to mixtures of monosulfonylated and disulfonylated products. However, allylmagnesium chloride and phenylmagnesium chloride provide the corresponding sulfones in excellent yields. Organocopper reagents were also found to yield sulfones upon treatment with arenesulfonyl fluorides. By utilizing this methodology, synthetically useful alkyl, (trimethylsilyl)methyl, and allyl sulfones are easily prepared in high yields.

Sulfones are of interest as intermediates in organic synthesis[1] and as pharmaceutical agents.[2] Common methods for the preparation of sulfones include oxidation of sulfides and sulfoxides, Friedel–Crafts sulfonylation of aromatic hydrocarbons, and alkylation of sulfinates.[1] Examples of the direct sulfonylation of organometallic reagents are rare.[3-7] A limited number of examples exist

Scheme I



in which *aryl* organometallic reagents (Ar'Met) are successfully sulfonylated with sulfonyl fluorides (eq 1).[6,8,9]



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