Stereoselective Construction of Tetrasubstituted Exocyclic Alkenes from the [4 + 2]-Cycloaddition of Vinylallenes

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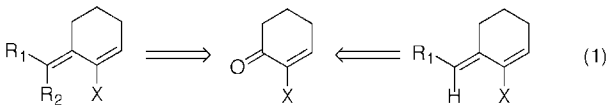
In the course of our synthetic studies on quassinoids[1] we required the stereoselective preparation of a tetrasubstituted exocyclic double bond of the type shown as structure **1** (eq 1, R_1, R_2, X ≠ H).[2] Starting from the



(1)

1 **2** **3**

corresponding 2-X-2-cyclohexen-1-one **2**, a wide range of methods were examined to no avail, including Wittig olefination, aldol condensation/elimination, McMurray coupling, addition of 2-propenyllithium followed by Claisen rearrangement or S_N2' displacements. Most of them either gave back starting material or decomposition products. Yet, we could prepare trisubstituted analogues **3** in high yields. Possibly the steric congestion experienced by the four substituents on this rather planar π-system was to blame. The stereoselective construction of tetrasubstituted exocyclic double bonds in general remains a challenge in organic synthesis. We herein disclose preliminary results on the [4 + 2]-cycloaddition of vinylallenes as a stereoselective route to tetrasubstituted exocyclic alkenes including very strained ones that are difficult to prepare by other methods.

Reich and co-workers reported vinylallene cycloadditions that led to trisubstituted exocyclic alkenes with excellent stereoselectivity.[3,4] The geometry of the alkenes was consistent with an approach of the dienophile from the least hindered face of the diene (**I**‡ in Figure 1). Others have reported on the use of intramolecular Diels−Alder cycloadditions of vinylallenes for natural product synthesis.[5−8] To the best of our knowledge, no report of intermolecular [4 + 2]-cycloaddition of vinylallenes to form unsymmetrically tetrasubstituted exocyclic double bonds has appeared in the literature.

We prepared vinylallenes **5a**,**b** and **8b**,**c**,**d** as depicted in Schemes 1 and 2.[9] Compounds **4a**−**d** were obtained from the addition of the appropriate alkynylmetal to

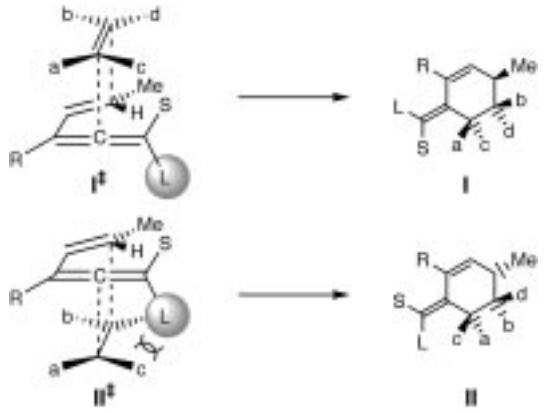
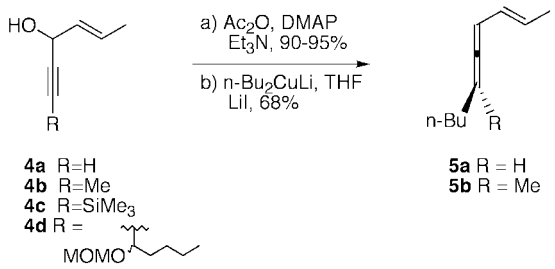
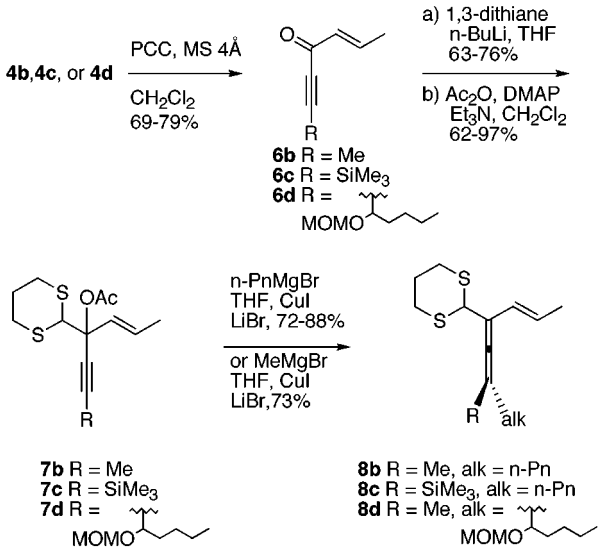


Figure 1. Exocyclic alkene geometries resulting from the two approaches on the vinylallenes.

Scheme 1



Scheme 2



crotonaldehyde. The resulting alcohols **4a** and **4b** were directly acetylated (Scheme 1) while alcohols **4b**−**d** were oxidized and reacted with the anion of 1,3-dithiane prior to acetylation to give acetates **7b**−**d**, respectively (Scheme 2). Displacement of each acetate with dialkylcuprates under strictly defined conditions led to vinylallenes **5** or **8**, respectively, with no or small amounts of byproducts from addition on the double bond.[3,10] Table 1 summarizes the results of the cycloaddition of each vinylallene with

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(1) For a review on the synthesis of quassinoids, see: Kawada, K.; Kim, M.; Watt, D. S. *Org. Prepr. Proc. Int.* **1989**, *21*, 521.

(2) Spino, C.; Liu, G.; Tu, N.; Girard, S. *J. Org. Chem.* **1994**, *59*, 5596.

(3) Reich, H. J.; Eisenhart, E. K.; Whipple, W. L.; Kelly, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 6432 and references therein.

(4) For a review on vinylallenes, see: Egenburg, I. Z. *Russ. Chem. Rev.* **1978**, *47*, 470.

(5) Okamura, W. H.; Curtin, M. L. *Synlett* **1990**, 1.

(6) Reich, H. J.; Eisenhart, E. K. *J. Org. Chem.* **1984**, *49*, 5282.

(7) Keck, G. E.; Kachensky, D. F. *J. Org. Chem.* **1986**, *51*, 2487.

(8) Deutsch, E. A.; Snider, B. B. *J. Org. Chem.* **1982**, *47*, 2682.

(9) All new compounds gave satisfactory NMR and mass spectral data.

(10) Macdonald, T.; Reagan, D. R. *J. Org. Chem.* **1980**, *45*, 4740.

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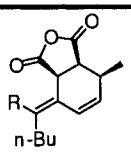
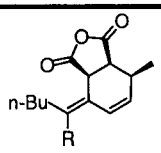
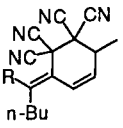
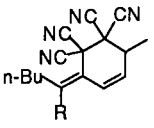
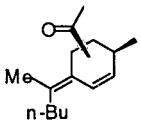
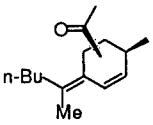
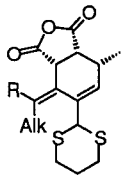
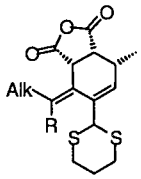
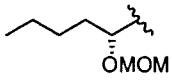
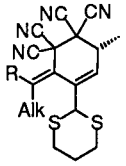
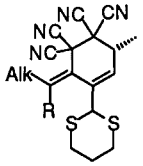
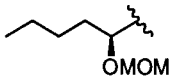
Table 1. [4 + 2]-Cycloadditions of Vinylallenes 5 and 8 in Toluene with Various Dienophiles

Entry	Vinyl allene	Dienophile[a] (T °C)	Products (racemic) *I*	*II*		Yield (%)[b]	*I*:*II*[c] (%)
1	**5a**	MA (25)			**9a** (R=H)	96	8:1
2	**5b**	MA (25)			**9b** (R=Me)	82	3:1
3	**5a**	TCE (25)			**10a** (R=H)	95	>49:1
4	**5b**	TCE (25)			**10b** + **15** (1:1, R=Me)	55	7:1[d]
5	**5b**	MVK[e]			**11** + **12** (1:1)	28	3:1
6	**8b**	MA (25)			**13b** (R=Me, Alk=n-Pn)	99	3:1
7	**8c**	MA (110)			**13c** (R=SiMe$_3$, Alk=n-Pn)	84	>1:49
8	(S,S)*-**8d**	MA (25)			**13d** (R=Me, Alk= )	91	9:1
9	**8b**	TCE (25)			**14b** (R=Me, Alk=n-Pn)	62	6:1
10	**8c**	TCE (110)			**14c** (R=SiMe$_3$, Alk=n-Pn)	45	>1:49
11	(R,S)*-**8d**	TCE (25)			**14d** (R=Me, Alk= )	88	>49:1

[a] See text for acronyms. [b] Isolated yield, unoptimized. [c] cf Figure 1. Ratio based on integration of signals in NMR or GC spectra of crude product. [d] **15** was a 2:1 mixture of isomers. [e] 40 °C in CH_2Cl_2 + Me_2AlCl.

various dienophiles. The reported yields are for isolated material, and though the maleic anhydride adducts could not be purified by chromatography, the crude material was of acceptable purity for identification. In the other cases, the isomers could be separated by chromatography and their structures were secured by spectral methods. The geometry of all exocyclic alkenes were inferred from X-ray single-crystal analyses on the major component of **14b**, **14c**, and **14d**.

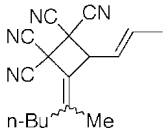
Trisubstituted alkenes **9a** and **10a** were obtained with high selectivity, in line with results published by Reich.[3] Vinylallenes **5b** and **8b** bearing a methyl and a straight *n*-alkyl chain reacted at room temperature in toluene in 5 days with tetracyanoethylene (TCE) or maleic anhydride (MA) to give good yields of separable isomers (entries 2, 4 and 6, 9). Those gave moderate but acceptable ratios of geometric isomers considering the small steric difference between a methyl and a simple *n*-alkyl chain. Vinylallenes **8c** and **8d** substituted with either a trimethylsilyl or a branched alkyl chain gave high yields and excellent ratios of geometric isomers (entries 7, 8 and 10, 11). The silyl-substituted allene required refluxing toluene for complete reaction. Vinylsilanes can be transformed into a host of vinylic functionalities and this route may indirectly lead to a large number of exocyclic alkenyl products in a highly stereoselective manner. We are currently undertaking these transformations. The X-ray analysis shows compound **14c** to be highly strained and its synthesis is noteworthy. In the crystal form, its exocyclic double bond twists by more than 20° to alleviate steric repulsion between the four substituents. Adducts **13** and **14** are all strained systems difficult to obtain by other methods.

TCE gave higher ratios of isomers than maleic anhydride, a result consistent with the endo approach of the latter, exposing the smaller hydrogens to the substituents on the allene (Figure 1, c = d = CN vs H). Less reactive dienophiles, such as methyl acrylate (MAcr), methyl vinyl ketone (MVK), and phenyl vinyl sulfone were slow to react at room temperature, but heating the vinylallenes for extended periods of time resulted in significant decomposition (except for **8c**). However, dimethylaluminum chloride catalyzed the cycloaddition with MAcr and MVK (entries 5). It was evident that two regioisomers **11** and **12** had formed in these cycloadditions, in contrast with what has been reported in simpler systems.[11−13] In the case of MVK, we could identify the four isomers by ^{1}H NMR and they consisted of a 1:1 ratio of the two regioisomers **11** and **12** each as the expected 3:1 mixture of geometrical double bond isomers.

Curiously, the reaction of vinylallene **5b** with TCE yielded the [2 + 2]-cycloadduct **15** along with the [4 + 2]-cycloadduct **10b**. The structures of the two separable isomers of **15** were ascertained by NMR spectroscopy and

(11) Bertrand, M.; Grimaldi, J.; Waegell, B. *Bull. Soc. Fr.* **1971**, 962.
(12) Yoshida, K.; Grieco, P. *Chem. Lett.* **1985**, 155.
(13) For a case of regioselectivity similar to ours see Santelli, M.; El Abed, D.; Jellal, A. *J. Org. Chem.* **1986**, *51*, 1199.

mass spectrometry. We did not observe any [2 + 2]-cycloadduct in the other reactions. Though the thermal [2 + 2]-cycloaddition of allenes is well-known, it is remarkable that this one occurs at room temperature.[14] Alternatively, this could be indicative of a biradical mechanism in this case.



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This preliminary study reveals the potential of the intermolecular Diels−Alder reaction of vinylallenes to selectively construct tetrasubstituted exocyclic double bonds on six-membered rings. Highly strained molecules can be prepared in this way. Further expansion and applications of this methodology are in progress and will be reported in due course.

Experimental Section

Reactions were performed under a dry nitrogen atmosphere with oven-dried glassware unless otherwise stated. Diethyl ether, hexanes, and tetrahydrofuran were distilled over sodium−benzophenone. Dichloromethane and triethylamine were distilled over calcium hydride. Flash chromatography was done using Merck Kieselgel silica gel 60 (230−400 mesh A. S. T. M.) Concentration of organic solutions implies evaporation on a rotary evaporator followed by pumping under reduce pressure (0.5 mmHg).

(*E*)-3-Hydroxy-4-hexen-1-yne (4a). Crotonaldehyde (4.14 mL, 50 mmol) was added to a solution of ethynylmagnesium bromide (100 mL, 50.0 mmol, 0.5 M/THF) at −78 °C. After 2 h of stirring, the mixture was poured into a solution of saturated ammonium chloride and extracted twice with diethyl ether. The combined organic layers were washed with water and brine, dried over magnesium sulfate, and concentrated. The crude product **4a** was obtained in 76% yield as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.73 (d, 3H, J = 6.5 Hz), 2.12 (bd, 1H, J = 4.8 Hz), 2.56 (d, 1H, J = 1.6 Hz), 4.82 (m, 1H), 5.59−5.66 (dm, 1H, J = 15.5 Hz), 5.92 (dq, 1H, J = 15.5, 6.5 Hz). IR ($CHCl_3$, cm^{-1}): 3594−3306 (bs), 3017 (m). LRMS (*m*/*z* (relative intensity)): 96 (M^+, 10), 81 (100), 67 (20), 53 (80). Exact mass calcd for C_6H_8O: 96.0575. Found: 96.0578.

(*E*)-4-Hydroxy-5-hepten-2-yne (4b). Propyne (1.54 mL, 27.2 mmol) was condensed into a flask containing 10 mL of dry THF at −78 °C, and 17 mL of *n*-butyllithium (23.6 mmol, 1.4 M/pentane) was added slowly. After 30 min of stirring, crotonaldehyde (1.5 mL, 18.1 mmol) was added by syringe. The yellow solution was quenched after 50 min at −78 °C with a solution of saturated ammonium chloride. The aqueous phase was extracted twice with diethyl ether. The combined organic layers were washed with water and brine, dried over magnesium sulfate, filtered, and concentrated to give 100% crude yield of alcohol **4b**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.70 (d, 3H, J = 6.6 Hz), 1.85 (d, 3H, J = 2.1 Hz), 1.98 (bd, 1H, J = 4.3 Hz), 4.76 (m, 1H), 5.59 (bdd, 1H, J = 15.1, 6.2 Hz), 5.84 (dq, 1H, J = 15.1, 6.6 Hz). IR ($CHCl_3$, cm^{-1}): 3596−3436, 3018. LRMS (*m*/*z* (relative intensity)): 110 (M^+, 10), 95 (100), 67 (50), 40 (50). Exact mass calcd for $C_7H_{10}O$: 110.0732. Found: 110.0736.

(*E*)-7-Methoxymethoxy-2-undecen-5-yn-4-ol (4d). Valeraldehyde (3.33 mL, 31.3 mmol) was slowly added to a solution of ethynylmagnesium bromide (67 mL of 0.5M in THF, 33.5 mmol) at −78 °C. The mixture was stirred for 45 min at −78 °C and then quenched with saturated aqueous ammonium chloride. The aqueous layer was separated then extracted three times with diethyl ether. The organic layers were combined and washed with water then with brine, dried over anhydrous magnesium sulfate, and filtered. Evaporation of the solvent in vacuo was followed by a Kugelrohr distillation (0.1 Torr, 80 °C) to yield 1-heptyn-3-ol (1.59 g, 44%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 4.36 (dt, 1H, J = 6.6, 1.6 Hz), 2.45 (d, 1H, J = 2.2 Hz), 1.95 (s, 1H), 1.76−1.68 (m, 2H), 1.49−1.29 (m, 4H), 0.91 (t, 3H, J = 7.1 Hz). IR (neat, cm^{-1}): 3550−3070 (bw), 3303 (ms). MS (*m*/*z*, intensity): 111 (M-1, 5), 79 (60), 70 (50), 55 (100), 41 (50). Exact mass calcd for $C_7H_{11}O$: 111.0810. Found: 111.0808.

A round-bottomed flask was charged with dichloromethane (30 mL), 1-heptyn-3-ol (1.36 g, 12.4 mmol), and dimethoxymethane (6.5 mL, 73.5 mmol) under nitrogen. The solution was cooled to 0 °C and was allowed to stir for 10 min. Then 100 mg of P_2O_5 was added while the reaction stirred vigorously. Every 10 min, 100 mg of P_2O_5 was added until the reaction was completed, as monitored by TLC. The mixture was then carefully added to 100 mL of an ice-cold saturated solution of aqueous sodium bicarbonate and the gummy residue remaining in the flask was also carefully washed with that same solution. The aqueous layer was separated and extracted three times with diethyl ether. The organic layers were combined then washed with brine, dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to yield a yellow oil. The oil was purified by Kugelrohr distillation (0.1 Torr, 90 °C) to yield 3-methoxymethoxy-1-heptyne (1.00 g, 53%) as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 4.94 (d, 1H, J = 6.8 Hz), 4.59 (d, 1H, J = 6.8 Hz), 4.31 (td, 1H, J = 6.6, 2.0 Hz), 3.38 (s, 3H), 2.40 (d, 1H, J = 2.1 Hz), 1.79−1.71 (m, 2H), 1.51−1.30 (m, 4H), 0.92 (t, 3H, J = 7.2 Hz). IR (neat, cm^{-1}): 3303 (ms), 1035 (s). MS (*m*/*z*, intensity): 155 (M − 1, 1), 111 (10), 99 (100), 55 (20), 45 (100). Exact mass calcd for $C_9H_{15}O_2$: 155.1072. Found: 155.1075.

3-Methoxymethoxy-1-heptyne (1.00 g, 6.4 mmol) was dissolved in tetrahydrofuran (3 mL) and cooled to −78 °C. A solution of *n*-butyllithium (3.2 mL, 2 M in pentane, 6.4 mmol) was then added dropwise. The mixture was stirred for 0.5 h at −78 °C and then crotonaldehyde (0.45 mL, 5.4 mmol) was slowly added. The mixture was stirred for 1.5 h and quenched with saturated aqueous ammonium chloride. The aqueous layer was separated and extracted three times with diethyl ether. The organic layers were combined, washed with water then with brine, dried over anhydrous magnesium sulfate, and filtered. Evaporation of the solvent in vacuo gave **4d** (1.22 g, 100%) as a slightly yellow oil used directly for the next reaction. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.87 (dq, 1H, J = 15.1, 7.0 Hz), 5.61 (bdd, 1H, J = 15.1, 6.3 Hz), 4.93 (d, 1H, J = 6.8 Hz), 4.85 (d, 1H, J = 6.3 Hz), 4.58 (d, 1H, J = 6.8 Hz), 4.37 (t, 1H, J = 6.3 Hz), 3.37 (s, 3H), 1.8−1.7 (m, 3H), 1.72 (d, 3H, J = 7.0 Hz), 1.50−1.30 (m, 4H), 0.92 (t, 3H, J = 7.1 Hz). IR (neat, cm^{-1}): 3550−3100 (mb), 1036 (s). MS (*m*/*z*, intensity): 181 (M − C_2H_5O, 4), 164 (5), 122 (70), 107 (100), 95 (20), 79 (45). Exact mass calcd for $C_{11}H_{17}O_2$:181.1228. Found: 181.1233.

(2*E*)-2,4,5-Decatriene (5a). Acetic anhydride (30 mL, 312 mmol) was added to a mixture of alcohol **4a** (15 g, 156 mmol), 4-(dimethylamino)pyridine (3.8 g, 31.2 mmol), and triethylamine (43 mL, 312 mmol) in 10 mL of dry dichloromethane. The reaction mixture was stirred for 5 h and was then poured into diethyl ether. The solution was washed with solutions of 1 N HCl and saturated sodium bicarbonate. Each separate aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and concentrated. Purification by flash chromatography (10% ethyl acetate/hexanes) gave 11.0 g of a colorless oil (52%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.74 (d, 3H, J = 6.6 Hz), 2.06 (s, 3H), 2.55 (d, 1H, J = 2.2 Hz), 5.55 (dm, 1H, J = 15.6 Hz), 5.80 (bd, 1H, J = 6.5 Hz), 6.01 (dq, 1H, J = 15.6, 6.6 Hz). IR ($CHCl_3$, cm^{-1}): 3307, 3027, 1736. LRMS (*m*/*z* (relative intensity)): 123 (($M - CH_3^+$), 10), 95 (25), 77 (80), 43 (100). Exact mass calcd for $C_7H_7O_2$: 123.0446. Found: 123.0448.

A flask containing copper iodide (1.70 g, 9.0 mmol), lithium iodide (1.20 g, 9.0 mmol), and 20 mL of dry tetrahydrofuran was cooled to −30 °C. A solution of *n*-butyllithium (11.5 mL, 17.9 mmol, 1.55 M in hexanes) was slowly added. The solution was left at −30 °C for 3 h. A solution of (*E*)-3-acetoxy-4-hexen-1-yne (1.03 g, 7.5 mmol) in 5 mL of dry THF was added. The mixture was stirred for 30 min at −30 °C and 1 h at 0 °C. The solution was then poured into a solution of saturated ammonium chloride. The aqueous layer was extracted three times with pentane. The combined organic layers were washed with water

(14) Landor, S. R.; Hopf, H.; Jacobs, T. L. *The Chemistry of Allenes, Reactions*; Academic Press: London, 1982; Vol. 2.

and brine, dried over magnesium sulfate, filtered, and concentrated. Purification by flash chromatography (1% ethyl acetate/pentane) gave the allene **5a** as a colorless oil (694 mg, 68%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.9 (m, 3H), 1.20−1.40 (m, 4H), 1.74 (dd, 3H, J = 6.6, 2.1 Hz), 1.95−2.05 (m, 2H), 5.37 (q, 1H, J = 6.6 Hz), 5.60 (dq, 1H, J = 14.1, 6.6 Hz), 5.7−5.9 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (q), 18.1 (q), 22.7 (t), 28.6 (t), 31.3 (t), 92.2 (d), 126.6 (d), 127.2 (d), 206.1 (s). IR ($CHCl_3$, cm^{-1}): 2960, 2931, 1698. LRMS (*m*/*z* (relative intensity)): 136 (M^+, 4), 127 (10), 108 (50), 94 (90), 79 (100). Exact mass calcd for $C_{10}H_{16}$: 136.1252. Found: 136.1247.

(*E*)-5-Hepten-2-yn-4-one (6b). The alcohol **4b** (500 mg, 4.5 mmol) was dissolved in 45 mL of dry dichloromethane. The mixture was cooled to 0 °C, and molecular sieves (1 g) were added. After 5 min of stirring, pyridinium chlorochromate (1.47 g, 6.81 mmol) was added portionwise and the mixture was stirred overnight. Activated charcoal was added and filtered through Celite. Celite was added to the filtrate and stirred for 5 min. The mixture was filtered over a pad of silica, activated charcoal, and Celite, yielding 384 mg (79%) of a colorless oil (**6b**). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.95 (d, 3H, J = 6.5 Hz), 2.03 (s, 3H), 6.13 (dd, 1H, J = 15.0, 2.7 Hz), 7.16 (dq, 1H, J = 15.0, 6.5 Hz). IR ($CHCl_3$, cm^{-1}): 3018, 1646, 1623. LRMS (*m*/*z* (relative intensity)): 110 (M^+, 12), 95 (100), 67 (50), 40 (50). Exact mass calcd for $C_7H_{10}O$: 110.0732. Found: 110.0736.

(*E*)-4-Acetoxy-4-(1,3-dithian-2-yl)-5-hepten-2-yne (7b). 1,3-Dithiane (642 mg, 5.3 mmol) was dissolved in 25 mL of THF and this solution was cooled to −40 °C. A solution of *n*-butyllithium (2.8 mL, 5.6 mmol, 2 M/pentane) was added slowly. The mixture was stirred for 2 h at −40 °C and was allowed to reach −20 °C. The mixture was immediately cooled back to −78 °C and the ketone **6b** (550 mg, 5.1 mmol) in 5 mL of THF was added. The reaction was stirred overnight at −60 °C. The mixture was poured into water and was extracted three times with chloroform. The combined organic layers were washed twice with water, once with a solution of 7% potassium hydroxide, once with water, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by flash chromatography (7% ethyl acetate/hexanes) to give **7b** (884 mg, 76%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.76 (d, 3H, J = 6.6 Hz), 1.92 (s, 3H), 1.96−2.08 (m, 2H), 2.69−2.79 (m, 2H), 3.06−3.17 (m, 3H), 3.95 (s, 1H), 5.63 (bd, 1H, J = 16.0 Hz), 6.15 (dq, 1H, J = 15.6, 6.6 Hz). IR ($CHCl_3$, cm^{-1}): 3582−3482, 3018. LRMS (*m*/*z* (relative intensity)): 228 (M^+, 5), 154 (7), 119 (110), 91 (75). Exact mass calcd for $C_{11}H_{16}OS_2$: 228.0643. Found: 228.0641.

Acetic anhydride (80 mL, 0.848 mmol) was added to a mixture of alcohol (97 mg, 0.424 mmol), 4-(dimethylamino)pyridine (10 mg, 0.0848 mmol), and triethylamine (120 mL, 0.848 mmol) in 350 mL of dry dichloromethane. The reaction mixture was stirred for 5 h and was then poured into diethyl ether. The solution was washed with solutions of 1 N HCl and saturated sodium bicarbonate. The separate aqueous layers were extracted twice with diethyl ether. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and concentrated to yield 72% (124 mg) of crude product **7b**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.77 (d, 3H, J = 6.6 Hz), 1.80−1.93 (m, 1H), 1.95 (s, 3H), 2.00−2.10 (m, 1H), 2.05 (s, 3H), 2.77−2.95 (m, 4H), 4.86 (s, 1H), 5.77 (bd, 1H, J = 15.5 Hz), 6.22 (dq, 1H, J = 15.5, 6.6 Hz). IR ($CHCl_3$, cm^{-1}): 2982, 1739. LRMS (*m*/*z* (relative intensity)): 270 (M^+, 2), 255 (5), 210 (75), 167 (50), 119 (100). Exact mass calcd for $C_{13}H_{18}O_2S_2$: 270.0748. Found: 270.0756.

(*E*)-4-(1,3-Dithian-2-yl)-6-methyl-2,4,5-undecatriene (8b). To a well-stirred mixture of lithium bromide (1.08 g, 12.4 mmol) and copper iodide (2.36 g, 12.4 mmol) in 25 mL of dry THF at 0 °C was added a solution of *n*-pentylmagnesium bromide (6.2 mL, 12.4 mmol, 2 M in diethyl ether) and the solution was stirred for 30 min. The propargylic substrate **7b** (558 mg, 2.1 mmol) in 5 mL of THF was added via syringe. After 2 h the reaction mixture was poured into a solution of saturated ammonium chloride. The aqueous layer was extracted twice with diethyl ether. The combined organic layers were dried over magnesium sulfate, filtered, and concentrated. Purification by flash chromatography (5% ethyl acetate/hexanes) gave 72% (418 mg) of **8b** as colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, 3H, J = 6.7 Hz), 1.25−1.33 (m, 4H), 1.46 (m, 2H), 1.76 (s, 3H), 1.77 (d, 3H, J = 5.5 Hz), 1.80−2.15 (m, 4H), 2.84 (dt, 2H, J = 15.5, 4.0 Hz), 2.97 (ddt, 2H, J = 15.5, 11.8, 2.6 Hz), 4.66 (s, 1H), 5.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1 (q), 18.3 (q), 19.2 (q), 22.5 (t), 25.6 (t), 27.1 (t), 31.6 (t), 2 × 31.8 (t), 34.2 (t), 48.0 (d), 104.3 (s), 105.3 (s), 125.0 (d), 126.4 (d), 202.7 (s). IR ($CHCl_3$, cm^{-1}): 2928, 1794. LRMS (*m*/*z* (relative intensity)): 282 (M^+, 7), 267 (10), 211 (50), 119 (100). Exact mass calcd for $C_{16}H_{26}S_2$: 282.1476. Found: 282.1482.

General Procedure for the Cycloaddition of Vinylallenes. To a round-bottomed flask under nitrogen were added the allene, the dienophile, and dry toluene. The mixture was stirred for several hours or days at room temperature or reflux. The solvent was then evaporated and purified as stated.

Cycloadduct 9a. Allene **5a** (84.9 mg, 0.62 mmol) and maleic anhydride (61.1 mg, 0.62 mmol) in 1.5 mL of dry toluene for 7 days at room temperature as described in the general procedure gave 139 mg of crude cycloaddition products **9a** (96%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.89 (t, 3H, J = 7.3 Hz), 1.26 (d, 3H, J = 7.7 Hz), 1.22−1.44 (m, 4H), 2.19 (q, 2H, J = 7.3 Hz), 2.72 (m, 1H), 3.37 (dd, 1H, J = 17.9, 9.0 Hz), 3.84 (d, 1H, J = 9.0), 5.77−5.85 (m, 2H), 6.44 (d, 1H, J = 9.3 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.9 (q), 17.4 (q), 22.2 (t), 27.4 (t), 28.7 (d), 31.3 (t), 45.0 (d), 45.2 (d), 65.8 (s), 122.2 (s), 123.6 (d), 132.1 (d), 134.2 (d), 171.6 (s). IR ($CHCl_3$, cm^{-1}): 3030, 2959, 1852, 1782. LRMS (*m*/*z* (relative intensity)): 234 (M^+, 10), 206 (15), 161 (20), 119 (30), 105 (100), 91 (90). Exact mass calcd for $C_{14}H_{18}O_3$: 234.1256. Found: 234.1261.

Cycloadduct 10b and 15. Allene **5b** (100 mg, 0.67 mmol) and tetracyanoethylene (85 mg, 0.67 mmol) in 1.5 mL of dry toluene for 5 days at room temperature as described in the general procedure gave after flash chromatography (7% ethyl acetate/hexanes) 58 mg of [4 + 2]-cycloaddition products **10b** (25%) and 70 mg of [2+ 2]-cycloaddition products **15** (30%). Cycloadducts **10b**: IR ($CHCl_3$, cm^{-1}): 2932, 2338, 1601, 1461, 1379. LRMS (*m*/*z* (relative intensity)): 278 (M^+, 70), 222 (100), 195 (50), 182 (75), 167 (45). Exact mass calcd for $C_{17}H_{18}N_4$: 278.1531. Found: 278.1523. **Major**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.94 (t, 3H, J = 7.2 Hz), 1.32−1.52 (m, 4H), 1.61 (d, 3H, J = 7.6 Hz), 2.29 (s, 3H), 2.29−2.41 (m, 2H), 3.21 (q, 1H, J = 7.0 Hz), 5.54 (dd, 1H, J = 10.4, 1.5 Hz), 6.62 (dd, 1H, J = 10.4, 2.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.8 (q), 17.5 (q), 22.2 (q), 22.5 (t), 30.2 (t), 35.9 (t) and (d), 42.1 (s), 48.5 (s), 109.4 (s), 109.7 (s), 109.9 (s), 111.2 (s), 115.7 (s), 123.9 (d), 124.6 (d), 150.5 (s). **Minor**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.98 (t, 3H, J = 7.0 Hz), 1.40−1.70 (m, 4H), 1.61 (d, 3H, J = 6.7 Hz), 2.02 (s, 3H), 2.38−2.50 (m, 1H), 2.65−2.77 (m, 1H), 3.15−3.27 (m, 1H), 5.55 (dd, 1H, J = 10.0, 1.5 Hz), 6.61 (dd, 1H, J = 10.0, 2.3 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.7 (q), 17.4 (q), 20.2 (q), 22.9 (t), 29.1 (t), 36.0 (d), 36.6 (t), 66.0 (s), 78 (s), 109.5 (s), 110.0 (s), 111.2 (s), 111.7 (s), 115.2 (s), 124.4 (d), 124.7 (d), 150.5 (s). Cycloadducts **15**: IR ($CHCl_3$, cm^{-1}): 3029, 2959, 2300, 1698, 1664, 1467, 1381. LRMS (*m*/*z* (relative intensity)): 278 (M^+, 5), 263 (10), 222 (100), 195 (45), 157 (80), 93 (90). Exact mass calcd for $C_{17}H_{18}N_4$: 278.1531. Found: 278.1526. **Major**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.91 (t, 3H, J = 6.7 Hz), 1.20−1.50 (m, 4H), 1.86 (d, 3H, J = 6.6 Hz), 1.95 (d, 3H, J = 2.3 Hz), 2.03 (t, 2H, J = 6.6 Hz), 4.39 (d, 1H, J = 8.5 Hz), 5.58−5.69 (m, 1H), 6.01 (dq, 1H, J = 15.0, 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.8 (q), 17.0 (q), 18.0 (q), 22.4 (t), 29.2 (t), 32.7 (t), 39.0 (s), 40.3 (s), 55.5 (d), 108.8 (s), 109.2 (s), 109.3 (s), 110.7 (s), 116.1 (s), 123.3 (d), 135.3 (d), 149.2 (s). **Minor**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.97 (t, 3H, J = 6.7 Hz), 1.35−1.60 (m, 4H), 1.72 (s, 3H), 1.88 (d, 3H, J = 6.7 Hz), 2.27 (t, 2H, J = 6.7 Hz), 4.39 (d, 1H, J = 6.8 Hz), 5.60−5.70 (m, 1H), 6.01 (dq, 1H, J = 15.0, 6.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.7 (q), 17.4 (q), 20.2 (q), 22.9 (t), 29.1 (t), 36.0 (d), 36.6 (t), 66.0 (s), 78 (s), 109.5 (s), 110.0 (s), 111.2 (s), 111.7 (s), 115.2 (s), 124.4 (d), 124.7 (d), 150.5 (s).

Cycloadduct 11 and 12. To a 10 mL flask under nitrogen were added allene **5b** (86.6 mg, 0.58 mmol), methyl vinyl ketone (91μL, 1.10 mmol), a solution of dimethylaluminum chloride (219 μL, 0.22 mmol, 1 M/diethyl ether), and 3 mL of dry dichloromethane. The mixture was stirred overnight at room temperature. The mixture was poured in saturated sodium bicarbonate and was extracted three times with diethyl ether. The combined organic layers were washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated. Purification by flash chromatography (eluted with 10% ethyl acetate: 90% hexanes) gives an oily mixture of **11** and **12** (41.9

mg, 28% yield). Cycloadducts **11**: IR ($CHCl_3$, cm^{-1}): 3022, 2960, 1706, 1461, 1358, 1224. LRMS (*m*/*z* (relative intensity)): 220 (M^+, 5), 205 (1), 177 (5), 135 (5), 119 (10), 85 (40), 43 (100). Exact mass calcd for $C_{15}H_{24}O$: 220.1827. Found: 220.1824. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.85 (d, 3H, J = 6.8 Hz), 0.90 (t, 3H, J = 7.0 Hz), 1.25−1.40 (m, 6H), 1.75 (s, 3H), 2.13 (d, 2H, J = 7.6 Hz), 2.30 (m, 1H), 2.51 (dd, 1H, J = 3.4, 15.8 Hz), 2.72−2.81 (m, 2H), 5.68 (dd, 1H, J = 5.0, 10.0 Hz), 6.40 (d, 1H, J = 10.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0 (q), 15.3 (q), 18.8 (q), 22.5 (t), 22.7 (t), 28.5 (q), 30.9 (t), 31.1 (d), 33.5 (t), 51.2 (d), 124.5 (d), 126.2 (s), 130.2 (d), 133.1 (s), 210.8 (s). Cycloadducts **12**: IR ($CHCl_3$, cm^{-1}): 3022, 2930, 1693, 1461, 1355, 1223. LRMS (*m*/*z* (relative intensity)): 220 (M^+, 7), 177 (20), 163 (20), 121 (30), 93 (60), 43 (100). Exact mass calcd for $C_{15}H_{24}O$: 220.1827. Found: 220.1830. **Minor**: ^1H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, 3H, J = 7.0 Hz), 0.97(d, 3H, J = 7.3 Hz), 1.20−1.40 (m, 4H), 1.82 (s, 3H), 1.85−2.05 (m, 4H), 2.15 (s, 3H), 2.22−2.35 (m, 1H), 3.49 (t, 1H, J = 6.0 Hz), 5.65 (dd, 1H, J = 10.0, 4.0 Hz), 6.48 (dd, 1H, J = 10.0, 2.0 Hz). **Major**: ^1H NMR ($CDCl_3$, 300 MHz): δ 0.92 (t, 3H, J = 7.0 Hz), 0.98 (d, 3H, J = 7.2 Hz), 1.23−1.46 (m, 4H), 1.61 (s, 3H), 1.72−1.80 (m, 1H), 1.95−2.02 (m, 1H), 2.11 (s, 3H), 2.15−2.31 (m, 3H), 3.41 (t, 1H, J = 6.8 Hz), 5.63 (dd, 1H, J = 3.6, 10.2 Hz), 6.50 (dd, 1H, J = 2.2, 10.2 Hz).

Cycloadduct 13b. Allene **8b** (69.6 mg, 0.25 mmol) and maleic anhydride (24.2 mg, 0.25 mmol) in 1 mL of dry toluene for 5 days at room temperature as described in the general procedure gave 93.0 mg of crude cycloaddition product **13b** (99%). **Major**: ^1H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, 3H, J = 6.3 Hz), 1.20−1.35 (m, 6H), 1.44 (d, 3H, J = 7.5 Hz), 1.7−2.3 (m, 5H), 1.93 (s, 3H), 2.80−2.97 (m, 4H), 3.15 (m, 1H), 3.32 (m, 1H), 4.39 (s, 1H), 6.12 (d, 1H, J = 4.1 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0 (q), 16.1 (q), 18.5 (q), 22.4 (t), 25.0 (t), 28.2 (t), 30.9 (d), 31.4 (t), 32.4 (t), 32.8 (t), 36.8 (t), 46.2 (d), 47.4 (d), 50.0 (d), 122.7 (s), 123.3 (s), 136.6 (d), 140.2 (s), 168.9 (s), 171.4 (s). **Minor**: ^1H NMR ($CDCl_3$, 300 MHz): δ same as major except, 1.90 (s, 3H), 6.15 (d, 1H, J = 4.1 Hz). IR ($CHCl_3$, cm^{-1}): 2929, 1779. LRMS (*m*/*z* (relative intensity)): 380 (M^+, 75), 309 (30), 273 (30), 41 (100). Exact mass calcd for $C_{20}H_{28}O_3S_2$: 380.1480. Found: 380.1475.

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Supporting Information Available: Proton NMR spectra for all compounds, and X-ray determinations of **14b**−**d** (ORTEP and tables of data), and experimental and characterization data for compounds **4c**, **5b**, **6c,d**, **7c,d**, **8c,d**, **9b**, **10a**, **13c,d**, **14b**−**d** (68 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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