Registry No. **3a**, 40200-18-8; **3c**, 71042-21-2; **3d**, 123333-21-1; **1**, 928-89-2; **4**, 592-42-7; **5**, 123333-22-2; **2**, 821-41-0; benzene, 71-43-2.

Supplementary Material Available: Physical data for compounds **3b-d** (1 page). Ordering information is given on any current masthead page.

A Stereoselective Route to 2-(Phenylthio)-1,3-butadienes

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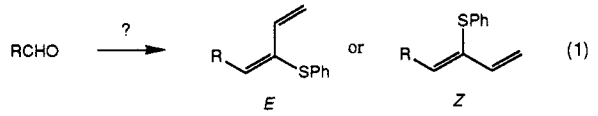
Sulfur-substituted 1,3-butadienes have found wide use in organic synthesis, particularly in Diels-Alder reactions, where they impart an added level of reactivity and regioselectivity to such cycloadditions.[1] These dienes also play an important role in the successful outcome of our recently developed method for the intramolecular cyclization of azides with 2-(phenylthio)-1,3-butadienes to afford 1-azabicyclo[3.3.0]oct-3-enes and 1-azabicyclo-[4.3.0]non-3-enes.[2] In our efforts to apply this cyclization methodology to alkaloid synthesis, we required an efficient method to prepare such dienes in a stereoselective fashion from aldehydes, as outlined in eq 1. We report herein a simple route to such dienes, which proceeds in high yield and with high stereoselectivity, affording either geometrical isomer.



E *Z* (1)

Several effective methods exist for the preparation of 2-(arylthio)-1,3-butadienes.[3-5] The most promising methods for dienes bearing a C-1 substituent, as required for our purposes, are those of Chou[1j-l,3b] and Yamamoto.[4] In Chou's work, extrusion of sulfur dioxide from 2-alkyl-3-(phenylthio)-3-sulfolenes in refluxing toluene affords 1-alkyl-2-(phenylthio)-1,3-butadienes with high *Z* selectivity, but does not allow access to the *E* isomers.[3b] Yamamoto has shown that condensation of the titanium reagent **1** with cyclohexanecarboxaldehyde produces 1-cyclohexyl-2-(phenylthio)-1,3-butadiene as a mixture of *E* and *Z* isomers (10:1).[4] We have used reagent **1** in our early work[2] but sought an alternative procedure for two reasons. First, ready access to either the pure *E* or pure *Z* isomer of the diene is not possible. Second, in our studies directed at natural product synthesis, we have found that more complex aldehydes which bear additional Lewis basic sites (e.g., ethers, esters, amides) give low yields of dienes with the titanium method. A major byproduct arises from addition at the γ-position of **1** (vide infra, Scheme II). Since complexation of the aldehyde oxygen to the titanium of **1** is probably an important event prior to C-C bond formation, we believe that additional Lewis basic sites interfere with the complexation and decrease the efficiency and α/γ regioselectivity of the reaction. We now report that the use of boron rather than titanium effectively addresses these limitations.

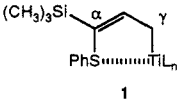


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Table I. Stereoselective Synthesis of 2-(Phenylthio)-1,3-butadienes from Aldehydes (RCHO) with Allylborane 4

diene[a]	R	isolated yield, %	6:7[b,c]
6a	n-C_5H_{11}	80	26:1
6b	n-C_8H_{17}	78	50:1
6c	i-C_3H_7	76	30:1
6d	c-C_6H_{11}	82	20:1
6e	Ph	58	1:1
6f	CH_2Ph	68	**6f** only
6g	$(CH_2)_3CH_2Br$	73	50:1
6h	$(CH_2)_2CH_2Br$	78	20:1
6i	$(CH_2)_3CH_2N_3$	79	**6i** only
6j	$(CH_2)_2CH_2N_3$	63	99:1
6k	(*E*)-CH=CHPh	66	**6k** only
7a	n-C_5H_{11}	92	1:50
7b	n-C_8H_{17}	74	**7b** only
7c	i-C_3H_7	83	1:50
7d	c-C_6H_{11}	87	**7d** only
7e	Ph	80	**7e** only
7f	CH_2Ph	84	**7f** only
7g	$(CH_2)_3CH_2Br$	82	**7g** only
7h	$(CH_2)_2CH_2Br$	86	**7h** only
7i	$(CH_2)_3CH_2N_3$	86	**7i** only
7j	$(CH_2)_2CH_2N_3$	80	**7j** only
7k	(*E*)-CH=CHPh	83	**7k** only

[a] Workup for **6** series: H_2SO_4. Workup for **7** series: 4 N NaOH. [b] Calculated by integration of the 300-MHz ^1H NMR spectrum of the crude reaction product. The spectra for the **7** series were measured on material obtained by direct evaporation of an aliquot in order to illustrate the inherently high stereoselectivity of the reaction. The spectra for the **6** series could not be obtained by direct evaporation of an aliquot due to acid-promoted decomposition, and thus had to be measured after neutralization and aqueous workup. This extra manipulation may explain the slightly lower selectivities observed for this series. [c] Where "only" is used, none of the other isomer is detected by 300-MHz ^1H NMR. It is estimated that this corresponds to a ratio of more than 200:1.

(1) (a) Review: Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753-786. Diels-Alder reactions using 2-thiosubstituted dienes: (b) Gundermann, K. D.; Holtmann, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 668. (c) Cohen, T.; Mura, A. J., Jr.; Shull, D. W.; Fogel, E. R.; Ruffner, R. J.; Falck, J. R. *J. Org. Chem.* **1976**, *41*, 3218-3219. (d) Hopkins, P. B.; Fuchs, P. L. *Ibid.* **1978**, *43*, 1208-1217. (e) Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3554-3572 and earlier work cited therein. (f) Trost, B. M.; Lavoie, A. C. *Ibid.* **1983**, *105*, 5057-5090. (g) Bridges, A. J.; Fischer, J. W. *Tetrahedron Lett.* **1983**, *24*, 445, 447. (h) Liotta, C. L.; Verbicky, J. W., Jr. *Ibid.* **1985**, *26*, 1395-1398. (i) Proteau, P. J.; Hopkins, P. B. *J. Org. Chem.* **1985**, *50*, 141-143. (j) Chan, T. H.; Prasad, C. V. C. *Ibid.* **1987**, *52*, 110-119 and earlier references therein. (k) Chou, T.; Lee, S.-J.; Peng, M.-L.; Sun, D.-J.; Chou, S.-S. P. *Ibid.* **1988** *53*, 3027-3031. (l) Chou, S.-S. P.; Tsai, C.-Y. *Ibid.* **1988**, *53*, 5305-5308. (m) McDougal, P. G.; Oh, Y.-I.; VanDerveer, D. *Ibid.* **1989**, *54*, 91-97. Diels-Alder using 1-thiosubstituted dienes: ref 1c and (n) Evans, D. A.; Bryan, C. A.; Sims, C. L. *J. Am. Chem. Soc.* **1972**, *94*, 2891. (o) Cohen, T.; Kosarych, A. *J. Org. Chem.* **1982**, *47*, 4005. (p) Kozikowski, A. P.; Huie, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 2923. (q) Overman, L. E.; Petty, C. B.; Ban, T.; Huang, G. T. *Ibid.* **1983**, *105*, 6335. (r) Ihara, M.; Kawaguchi, A.; Chihiro, M.; Fukumoto, K.; Kametani, T. *J. Chem. Soc., Chem. Commun.* **1986**, 671.

(2) Pearson, W. H.; Celebuski, J. E.; Poon, Y.-F.; Dixon, B. R.; Glans, J. H. *Tetrahedron Lett.* **1986**, *52*, 6301-6304.

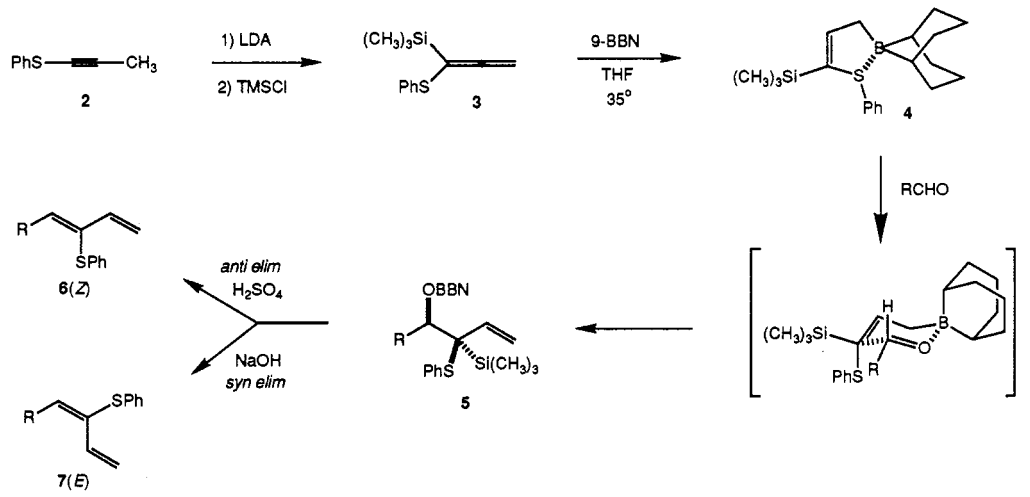
(3) From 3-(phenylthio)-3-sulfolenes by extrusion of sulfur dioxide: (a) References 1b,d,f,h,i,k,l. (b) Chou, S.-S. P.; Liou, S.-Y.; Tsai, C.-Y.; Wang, A.-J. *J. Org. Chem.* **1987**, *52*, 4468-4471.

(4) (a) Ikeda, Y.; Furuta, K.; Meguriya, N.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1982**, *104*, 7663-7665. (b) Furuta, K.; Ikeda, Y.; Meguriya, N.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2781-2790. This work also describes one example of a route to the *Z* isomer. Titanium-mediated addition of [1-(phenylthio)allyl]lithium to cyclohexanecarboxaldehyde affords selectively the *erythro*-β-hydroxy sulfide. Treatment of this compound with *n*-BuLi, methanesulfonyl chloride, and then *t*-BuLi afforded *Z*-**6d**. This method has not been useful in our hands for more sensitive and complex aldehydes.

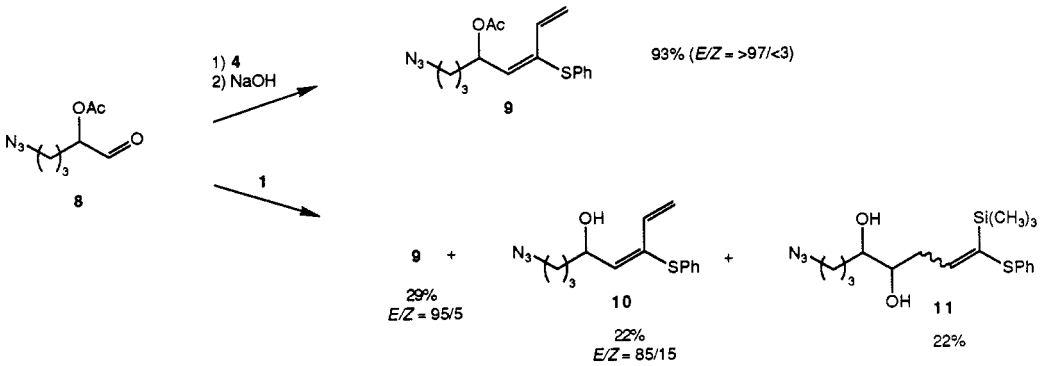
(5) Other methods: (a) References 1c,e,g,j. (b) Blatcher, P.; Grayson, J. I.; Warren, S. *J. Chem. Soc., Chem. Commun.* **1978**, 657. (c) Pariza, R. J.; Fuchs, P. L. *J. Org. Chem.* **1985**, *50*, 4252-4266.

0022-3263/89/1954-5814$01.50/0

Scheme I



Scheme II



Results and Discussion

Matteson,[6] Yamamoto,[7] and Wang,[8] have reported that condensations of trimethylsilyl-substituted allylboronates or allylboranes with aldehydes proceed with high diastereoselectivity, and that the resultant β-hydroxysilanes undergo loss of trimethylsilanol to give dienes.[9,10] Under basic workup conditions, a syn elimination of trimethylsilanoxide affords one diene geometry, while acid workup produces the complementary isomer.[11] We have found that this strategy provides an excellent route to the desired dienes when the allyl borane is substituted appropriately with a phenylthio group.

Scheme I shows the general approach. Allene **3** is available from 1-(phenylthio)-1-propyne (**2**)[12] by deprotonation[13] with lithium diisopropylamide (LDA) and quenching with chlorotrimethylsilane (TMSCl).[14] Hydroboration of **3** with 9-borabicyclo[3.3.1]nonane (9-BBN)[15] at 35 °C produces the allylborane **4**, which is not isolated. Although the geometry of **4** is unknown, the facile allylic rearrangement of allylic dialkylboranes[15a] most likely allows formation of the more stable *Z* isomer.[16] Condensation of **4** with aldehydes proceeds at room temperature to presumably generate an intermediate β-boronoxysilane **5**, which was treated with sulfuric acid to produce the *Z* diene **6**. Alternatively, workup with 4 N sodium hydroxide gave the *E* diene **7** (Table I). With the exception of **6e**, these reactions show very high stereoselectivity, with the minor isomer often being undetectable by examination of the high-field ^{1}H NMR spectrum of the crude reaction mixture. This stereoselectivity is probably a result of the strong preference for allyl borane reactions to proceed through a chair transition state,[6-9] selectively producing

(6) Tsai, D. J. S.; Matteson, D. S. *Tetrahedron Lett.* **1981**, *22*, 2751–2752.

(7) Yamamoto, Y.; Saito, Y.; Maruyama, K. *J. Organomet. Chem.* **1985**, *292*, 311–318.

(8) (a) Liu, C.; Wang, K. K. *J. Org. Chem.* **1986**, *51*, 4733–4734. (b) Liu, C. Ph.D. Thesis, University of West Virginia.

(9) General references for allylborane and allylboronate additions to carbonyl compounds: (a) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (b) Matteson, D. S. *Synthesis* **1986**, 973–985. (c) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243–249. (d) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988. (f) Bubnov, Y. N.; Zheludeva, V. I.; Ignatenko, A. V. *J. Organomet. Chem.* **1989**, *359*, 151–158 and references therein.

(10) Related diene syntheses using silane-substituted allylic organometallics: (a) Chan, T.-H.; Li, J.-S. *J. Chem. Soc., Chem. Commun.* **1982**, 969–970. (b) Sato, F.; Suzuki, Y.; Sato, M. *Tetrahedron Lett.* **1982**, *23*, 4589–4592. (c) Reetz, M. T.; Wenderoth, B. *Ibid.* **1982**, *23*, 5259–5262. (d) Murai, A.; Abiko, A.; Shimada, N.; Masamune, T. *Ibid.* **1984**, *4951*–4954. (e) Ikeda, Y.; Ukai, J.; Ikeda, N.; Yamamoto, H. *Tetrahedron* **1987**, *43*, 731–741 and earlier references therein.

(11) (a) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464–1468. (b) Chan, T.-H. *Acc. Chem. Res.* **1977**, *10*, 442–448. (c) Ager, D. J. *Synthesis* **1984**, 384–398. (d) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: New York, 1988.

(12) (a) Pourcelot, G.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1966**, 3016–3024. (b) Pourcelot, G.; Catiot, P.; Willemant, A. *C. R. Acad. Sci.* **1961**, *252*, 1630.

(13) (a) Brandsma, L.; Jonker, C.; Berg, M. H. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 560–566. (b) Bridges, A. J.; Thomas, R. D. *J. Chem. Soc., Chem. Commun.* **1983**, 485–486.

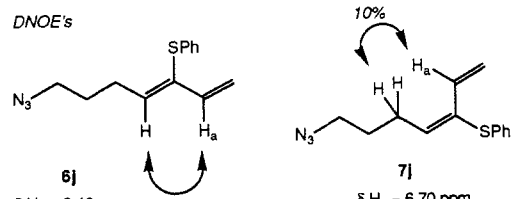
(14) An alternate approach to **3** involving metalation of 1-(phenylthio)-1,2-propadiene[13] followed by silylation was found to be less efficient and direct. Other workers have also noted the greater convenience of **2** as a source of lithioallene.[13b]

(15) (a) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1977**, *132*, 9–27. (b) Brown, H. C.; Liotta, R.; Kramer, G. W. *J. Am. Chem. Soc.* **1979**, *101*, 2966–2970. (c) See also ref 8 and 9d,f.

(16) The *Z* isomer may be less sterically crowded and may benefit by internal coordination of sulfur to boron. Alternatively, **4** may be an equilibrating mixture,[15a] from which only the *Z* isomer reacts with an aldehyde. Yamamoto[7] has studied the additions of silicon- and sulfur-substituted allylboranes to aldehydes, and our conclusions about the geometry of **4** are consistent with these findings.

diastereomer **5**. Dienes **6** and **7** isomerize slowly upon standing or upon extended contact with silica gel,[2,4b] and the actual isolated E/Z ratios depend on the method of purification. Using rapid flash chromatography,[17] isolation of dienes with 0–5% change in the values reported in Table I is routinely possible.

The geometry of the dienes was ascertained by difference NOE spectroscopy on dienes **6j** and **7j**. The critical enhancements are shown below. This assignment may be conveniently generalized to all of the examples in Table I by noting the chemical shift of H_a. When the ^1H NMR spectrum is measured in deuteriochloroform, H_a in the E isomers is generally 0.26–0.30 ppm further downfield than in the Z isomers.



Access to other 2-heterosubstituted 1,3-butadienes may be possible with this methodology, although initial attempts to hydroborate more hindered allenes or oxygen-substituted allenes have been unsuccessful.[18]

The allylborane method also works efficiently with aldehydes bearing Lewis basic sites. Aldehyde **8**,[22] which bears an acetoxy group, is smoothly converted to diene **9** with the allylborane **4** (Scheme II). In contrast, the titanium based reagent **1**[4] leads to roughly equal proportions of the desired diene **9**, deacetylated diene **10**, and the γ-adduct **11**.

In conclusion, the allylborane route to 1-substituted 2-(phenylthio)-1,3-butadienes **6** and **7** proceeds in good yield and allows access to either diene geometry with high stereoselectivity. The reaction displays good chemoselectivity, proceeding in the presence of other electrophilic and/or Lewis basic groups (bromides, esters, azides).

Experimental Section

General. Reagents and starting materials were generally obtained from commercial suppliers and were used without further purification. Aldehydes were freshly distilled prior to use with the exception of phenylacetaldehyde, which was used as obtained commercially. Chlorotrimethylsilane was distilled from tri-*n*-butylamine. Ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl immediately prior to use. Methylene chloride and diisopropylamine were distilled from calcium hydride. All reactions were conducted under a nitrogen atmosphere unless otherwise noted. All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, with chemical shifts being reported in ppm downfield from tetramethylsilane as an internal standard. ^1H NMR spectra were recorded at 300 or 360 MHz. ^{13}C NMR spectra were recorded at 75 or 90 MHz. Multiplicities are reported as s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet; b, broad. Infrared spectra were recorded on FT-IR instruments, either neat between NaCl plates, or in the solvent indicated. Low- and high-resolution mass spectra data (MS, HRMS) are reported as m/e, with the intensity expressed in parentheses as percent of the base peak. Electron impact spectra were obtained at 70 eV. Elemental analyses were performed by Spang Microanalytical Laboratory at Eagle Harbor, MI, Galbraith Laboratories, Inc., at Knoxville, TN, or the Microanalytical Laboratory operated by the Department of Chemistry, University of Michigan, Ann Arbor, MI. Flash chromatography refers to liquid chromatography on silica gel according to the method of Still.[19] Analytical thin-layer chromatography was performed on precoated silica gel plates (Merck 60 F-254). Gas chromatography was performed on a Hewlett-Packard 5890 instrument equipped with a methylsilicone column (5 m × 0.53 mm, 2.65 μm film thickness) using a temperature program beginning at 100 °C (2 min), and then 40 °C/min to 200 °C.

1-(Phenylthio)-1-(trimethylsilyl)-1,2-propadiene (3). To a well-stirred solution of freshly distilled diisopropylamine (14.0 mL, 10.1 g, 0.10 mol) in THF (450 mL) at 0 °C was added *n*-butyllithium (40.0 mL of a 2.5 M solution in hexanes, 0.10 mol) dropwise over 15 min. After 1 h, the solution was cooled to −75 °C, and a solution of freshly distilled 1-(phenylthio)-1-propyne (**2**)[12a] (14.8 g, 0.10 mol) in THF (10 mL) was added within a 10-s period through a stainless steel needle with the tip immersed well within the reaction solution. After 8 min, chlorotrimethylsilane (12.7 mL, 10.9 g, 0.10 mol) was added within a 10-s period, again with a needle immersed within the reaction solution. After 30 min, the mixture was quenched at −75 °C with saturated aqueous ammonium chloride (25 mL), diluted with pentane (250 mL), and allowed to warm to room temperature. The organic phase was washed with water (3 × 35 mL) and brine (3 × 35 mL), dried (Na_2SO_4), and concentrated in vacuo to give 22.0 g of a pale yellow oil. Gas chromatography showed this material to be 76% pure **3** (retention time 3.98 min), accompanied by 9% 1-(phenylthio)-1,2-propadiene (2.92 min) and 11% 3,3-bis(trimethylsilyl)-1-(phenylthio)-1-propyne (5.85 min). Distillation gave 13.6 g (62%) of **3** as a colorless oil (bp 49.5–52 °C at 0.04 mmHg), which was >95% pure by GC analysis: IR (film) 2360 (m), 2341 (w), 1922 (s), 1653 (w), 1582 (m), 1476 (m), 1438 (m), 1249 (s), 1178 (w), 1024 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.42–7.38 (m, 2 H), 7.30–7.26 (m, 3 H), 4.55 (s, 2 H), 0.16 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 209.44 (s), 135.24 (s), 131.46 (d), 128.90 (d), 126.85 (d), 92.78 (s), 73.00 (t), −1.50 (q) ppm; HRMS (70 eV) m/e (rel intensity) 220 (M^+, 6.4), 147 (5.4), 130 (9.4), 115 (9.4), 109 (6.5), 103 (3.6), 91 (4.1), 73 (100), 45 (13.8), 43 (11.2), 40 (6.0); calcd for $C_{12}H_{16}SSi$ 220.0742, found 220.0741.

General Procedure for the Condensation of Allylborane 4 with Aldehydes. Procedure A, Acidic Workup: (*Z*)-3-(Phenylthio)-1,3-nonadiene (6a). To 1-(phenylthio)-1-(trimethylsilyl)-1,2-propadiene (**3**) (115 mg of 95% pure allene, 0.50 mmol) was added 9-borabicyclo[3.3.1]nonane (9-BBN, 0.50 M in THF, 1.0 mL, 0.50 mmol) at room temperature. The mixture was stirred at 35 °C for 2 h to complete the formation of the allylborane **4**. After cooling to room temperature, this solution was added dropwise[23] via syringe to a stirred solution of hexanal (50 mg, 0.50 mmol) in tetrahydrofuran (0.5 mL) at 0 °C. The ice bath was removed, and the reaction mixture was allowed to stir for 2 h. Concentrated sulfuric acid (1 drop) was added, and the reaction mixture was allowed to stir for 2 h and then diluted with petroleum ether (20 mL). The organic phase was washed with saturated sodium bicarbonate (5 mL), dried (Na_2SO_4), and concentrated in vacuo. Flash chromatography (petroleum ether) gave 93 mg of **6a** (80%): R_f 0.47 (2% ether/petroleum ether); IR (neat): 1624 (m), 1585 (m), 1478 (s), 1439 (m), 908 (s), 738 (s), 688 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.08–7.27 (m, 5 H), 6.45 (dd, J = 16.7, 10.5 Hz, 1 H), 6.34 (t, J = 7.4 Hz, 1 H), 5.57 (b d, J = 16.7 Hz, 1 H), 5.07 (b d, J = 10.4 Hz, 1 H), 2.49 (q, J = 7.4 Hz, 2 H), 1.26–1.50 (m, 6 H), 0.86–0.92 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.66 (d), 137.10 (d), 136.63 (s), 131.50 (s), 128.66 (d), 127.07 (d), 124.97 (d), 115.79 (t), 31.52 (t), 30.36 (t), 28.72 (t), 22.47

(17) These dienes isomerize slowly at or above room temperature, but the isomerization is slow enough to allow purification and further use.

(18) For example, 1-(trimethylsilyl)-1-(phenylthio)-1,2-hexadiene and 1-(trimethylsilyl)-1-(benzyloxy)-1,2-propadiene failed to hydroborate with a variety of dialkylboranes, even at elevated temperature.

(19) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(20) Prepared from tetrahydrofuran or tetrahydropyran by a modification of the two-step procedure: Kulkarni, S. V.; Patil, V. D. *Heterocycles* **1982**, *18*, 163. Instead of isolation of the bromoalcohols from the BBr_3 reaction, they were directly oxidized with PCC/alumina; see: Cheng, Y.-S.; Liu, W.-L.; Chen, S. *Synthesis* **1980**, 223. This method was also used for the synthesis of 5-azidopentanal (see the Experimental Section).

(21) Hudlicky, T.; Frazier, J. O.; Seoane, G.; Tiedje, M.; Seoane, A.; Kwart, L. D.; Beal C. *J. Am. Chem. Soc.* **1986**, *108*, 3755–3762.

(22) Prepared from 4-azidobutanal: (i) vinylmagnesium bromide, THF, 0 °C, and then acetic anhydride quench; (ii) ozone, methanol, −78 °C, and then dimethyl sulfide workup.

(23) Addition of the aldehyde in THF to a 0 °C solution of the allylborane gives the same result and may be more convenient in some cases.

(t), 13.98 (q) ppm; MS *m/e* (rel intensity) 235 (M^+ + 3, 1) 234 (M^+ + 2, 5), 233 (M^+ + 1, 16), 232 (M^+, 86) 175 (100), 161 (40), 142 (47), 123 (43), 110 (48), 91 (45), 81 (90), 67 (70); HRMS calcd for $C_{15}H_{20}S$ 232.1286, found 232.1274.

General Procedure B, Basic Workup: (*E*)-3-(Phenylthio)-1,3-nonadiene (7a). The above procedure was repeated exactly as for **6a**, except that 4 N sodium hydroxide (5 drops) was added instead of concentrated sulfuric acid. The mixture was allowed to stir for 2 h at room temperature and was then diluted with petroleum ether (20 mL). The organic phase was washed with water (3 × 1 mL) and brine (2 mL), dried (Na_2SO_4), and concentrated in vacuo. Flash chromatography (SiO_2, petroleum ether) gave 115 mg (92%) of **7a**: R_f 0.47 (2% ether/petroleum ether); IR (neat) 1620 (w), 1584 (m) 1479 (s), 1439 (m), 1024 (m), 738 (s), 689 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.06–7.33 (m, 5 H), 6.72 (ddd, J = 16.5, 10.5, 1 Hz, 1 H), 6.24 (b t, J = 7.5 Hz, 1 H), 5.67 (b d, J = 16.5 Hz, 1 H), 5.21 (dt, J = 10.5, 1.5 Hz, 1 H), 2.35 (q, J = 7.5 Hz, 2 H), 1.27–1.54 (m, 6 H), 0.90 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.33 (d), 136.98 (s), 130.35 (d), 130.18 (s), 128.68 (d), 127.88 (d), 125.41 (d), 118.43 (t), 31.47 (t), 29.01 (t), 28.93 (t), 22.49 (t), 14.02 (q) ppm; MS *m/e* (rel intensity) 235 (M^+ + 3, 0.8), 234 (M^+ + 2, 6), 233 (M^+ + 1, 18), 232 (M^+, 98), 175 (58), 147 (32), 122 (41), 110 (38), 93 (61), 81 (100), 77 (50), 67 (61), 41 (70); HRMS calcd for $C_{15}H_{20}S$ 232.1286, found 232.1284. The following dienes were prepared according to the above general procedures. For the **6** series (*Z*-dienes), acidic workup A was used. For the **7** series (*E*-dienes), basic workup B was used.

(*Z*)-3-(Phenylthio)-1,3-dodecadiene (6b) was prepared on a 0.50-mmol scale from nonanal in 78% yield: R_f 0.51 (2% ether/petroleum ether); IR (neat) 1478 (m), 1466 (m), 1439 (m), 1025 (m), 979 (m), 908 (m), 738 (s), 688 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.07–7.26 (m, 5 H), 6.44 (dd, J = 10.5, 16.5 Hz, 1 H), 6.33 (t, J = 7.5 Hz, 1 H), 5.54 (d, J = 16.5 Hz, 1 H), 5.05 (d, J = 10.5 Hz, 1 H), 2.47 (q, J = 7.5 Hz, 2 H), 1.22–1.49 (m, 12 H), 0.89 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 300 MHz) δ 144.81 (d), 137.09 (d), 136.64 (s), 131.42 (s), 128.68 (d), 127.02 (d), 124.96 (d), 115.80 (t), 31.82 (t), 30.37 (t), 29.37 (t), 29.32 (t), 29.20 (t), 29.01 (t), 22.63 (t), 14.07 (q) ppm; MS *m/e* (rel intensity) 277 (M^+ + 3, 0.2), 276 (M^+ + 2, 2), 275 (M^+ + 1, 5), 274 (M^+, 24), 246 (1), 197 (5), 175 (62), 161 (24), 147 (24), 142 (24), 135 (18), 123 (23), 109 (64), 95 (67), 81 (54), 67 (69), 55 (47), 41 (100); HRMS calcd for $C_{18}H_{26}S$ 274.1755, found 274.1761.

(*E*)-3-(Phenylthio)-1,3-dodecadiene (7b) was prepared on a 0.50-mmol scale from nonanal in 74% yield: R_f 0.51 (2% ether/petroleum ether); IR (neat) 1584 (m), 1479 (s), 1088 (w), 1025 (w), 738 (s), 689 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.09–7.28 (m, 5 H), 6.71 (ddt, J = 16.7, 10.5, 1 Hz, 1 H), 6.23 (b t, J = 7.5 Hz, 1 H), 5.65 (dt, J = 16.7, 1 Hz, 1 H), 5.20 (b d, J = 10.5 Hz, 1 H), 2.34 (q, J = 7.5 Hz, 2 H), 1.25–1.5 (m, 10 H), 0.89 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.47 (d), 136.99 (s), 130.33 (d), 130.10 (s), 128.70 (d), 127.83 (d), 125.41 (d), 118.44 (t), 31.83 (t), 29.37–29.01 (m), 22.65 (t), 14.07 (q) ppm; MS *m/e* (rel intensity) 276 (M^+ + 2, 5), 275 (M^+ + 1, 19), 274 (M^+, 100), 259 (2), 207 (19), 197 (34), 189 (10), 175 (21), 164 (24), 147 (11), 135 (12), 109 (33), 95 (47), 79 (64), 67 (52), 55 (51), 41 (92); HRMS calcd for $C_{18}H_{26}S$ 274.1755, found 274.1761.

(*Z*)-3-(Phenylthio)-5-methyl-1,3-hexadiene (6c) was prepared on a 0.80-mmol scale from isobutyraldehyde in 76% yield: R_f 0.52 (2% ether/petroleum ether); IR (neat) 1625 (m), 1584 (m), 1479 (s), 1465 (m), 1440 (m), 1025 (m), 980 (m), 738 (s), 689 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.08–7.28 (m, 5 H), 6.41 (ddd, J = 16.5, 10.5, 0.8 Hz, 1 H), 6.15 (b d, J = 9 Hz, 1 H), 5.56 (b d, J = 16.5 Hz, 1 H), 5.07 (b d, J = 10.5 Hz, 1 H), 3.10–3.27 (m, 1 H), 1.05 (d, J = 6.5 Hz, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.52 (d), 137.10 (d), 136.83 (s), 129.20 (s), 128.79 (d), 127.07 (d), 125.07 (d), 116.17 (t), 29.75 (d), 22.45 (q) ppm; MS *m/e* (rel intensity) 207 (M^+ + 3, 0.5), 206 (M^+ + 2, 4), 205 (M^+ + 1, 11), 204 (M^+, 60), 189 (16), 161 (13), 147 (16), 127 (12), 109 (17), 95 (75), 91 (22), 79 (100), 77 (60), 67 (44), 55 (40), 41 (58), 39 (66); HRMS calcd for $C_{13}H_{16}S$ 204.0973, found 204.0975.

(*E*)-3-(Phenylthio)-5-methyl-1,3-hexadiene (7c) was prepared on a 0.80-mmol scale from isobutyraldehyde in 83% yield: R_f 0.52 (2% ether/petroleum ether); IR (neat) 1621 (w), 1583 (m), 1479 (s), 1465, (m), 1440 (m), 1025 (m), 977 (m), 738 (s), 689 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.08–7.40 (m, 5 H), 6.73 (ddd, J = 16.8, 10.5, 0.7 Hz, 1 H), 6.09 (dt, J = 9.8, 0.7 Hz, 1 H), 5.66 (dm, J = 16.8 Hz, 1 H), 5.20 (dt, J = 10.6, 1.5 Hz, 1 H), 2.93 (m, 1 H), 1.08 (d, J = 6.6 Hz, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.33 (d), 137.00 (s), 130.31 (d), 128.67 (d), 128.15 (s), 127.62 (d), 125.33 (d), 118.57 (t), 28.33 (d), 22.64 (q) ppm; MS *m/e* (rel intensity) 207 (M^+ + 3, 0.5), 206 (M^+ + 2, 4), 205 (M^+ + 1, 12), 204 (M^+, 70), 189 (17), 161 (15), 147 (16), 127 (13), 110 (17), 95 (76), 91 (21), 79 (100), 77 (56), 67 (45), 55 (44), 41 (58); HRMS calcd for $C_{13}H_{16}S$ 204.0972, found 204.0972.

(*Z*)-1-Cyclohexyl-2-(phenylthio)-1,3-butadiene (6d) was prepared on a 0.80-mmol scale from cyclohexanecarboxaldehyde in 82% yield: R_f 0.58 (2% ether/petroleum ether); IR (neat) 1624 (m), 1584 (s), 1478 (s), 1447 (s), 1440 (s), 979 (s), 907 (s), 901 (s), 738 (s), 689 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 7.10–7.28 (m, 5 H), 6.40 (dd, J = 16.5, 10.5 Hz, 1 H), 6.17 (d, J = 9.5 Hz, 1 H), 5.54 (d, J = 16.5 Hz, 1 H), 5.06 (d, J = 10.5 Hz, 1 H), 2.88 (m, 1 H), 1.67–1.76 (m, 5 H), 1.14–1.35 (m, 5 H) ppm; ^{13}C NMR ($CDCl_3$, 90 MHz) δ 150.03 (d), 136.96 (d), 136.76 (s), 129.34 (s), 128.67 (d), 127.04 (d), 124.96 (d), 116.02 (t), 39.22 (d), 32.46 (t), 25.87 (t), 25.52 (t) ppm; MS, *m/e* (rel intensity): 247 (M^+ + 3, 0.8), 246 (M^+ + 2, 6), 245 (M^+ + 1, 19), 244 (M^+, 100), 201 (11), 167 (36), 147 (30), 135 (74), 129 (39), 109 (22), 105 (23), 91 (88) 77 (53), 67 (45); HRMS calcd for $C_{16}H_{20}S$ 2449.1285, found 244.1284.

(*E*)-1-Cyclohexyl-2-(phenylthio)-1,3-butadiene (7d) was prepared on a 0.80-mmol scale from cyclohexanecarboxaldehyde in 87% yield: R_f 0.54 (2% ether/petroleum ether); IR (neat) 1620 (w), 1584 (m), 1479 (s), 1447 (m), 975 (m), 738 (s), 689 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.10–7.35 (m, 5 H), 6.74 (ddd, J = 17, 10.5, 0.5 Hz, 1 H), 6.11 (b d, J = 9.5 Hz, 1 H), 5.67 (dq, J = 17, 0.5 Hz, 1 H), 5.20 ndt, J = 10.5, 0.5 Hz, 1 H), 2.61 (m, 1 H), 1.66–1.82 (m, 5 H), 1.12–1.43 (m, 5 H) ppm; ^{13}C NMR ($CDCl_3$, 90 MHz) δ 149.12 (d), 137.10 (s), 130.46 (d), 128.67 (d), 128.40 (s), 127.52 (d), 125.28 (d), 118.45 (t), 38.06 (d), 32.69 (t), 25.79 (t), 25.61 (t) ppm; MS *m/e* (rel intensity) 247 (M^+ + 3, 0.8), 246 (M^+ + 2, 6), 245 (M^+ + 1, 19), 244 (M^+, 100), 210 (10), 167 (68), 147 (27), 135 (67), 105 (25), 91 (90), 77 (56), 67 (46); HRMS calcd for $C_{16}H_{20}S$ 244.1285, found 244.1285.

(*Z*)-1-Phenyl-2-(phenylthio)-1,3-butadiene (6e) was prepared on a 1.00-mmol scale from benzaldehyde in 58% yield with workup A, as an inseparable 1:1 mixture of *E* and *Z* isomers: R_f 0.26 (2% ether/petroleum ether). For *Z* isomer: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.68–7.73 (m, 2 H), 7.10–7.40 (m, 9 H), 6.57 (dd, J = 17, 10.5 Hz, 1 H), 5.72 (b d, J = 17 Hz, 1 H), 5.21 (b d, J = 10.5 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.76, 138.09, 136.12, 126.04, 131.42, 130.03, 128.94, 128.38, 127.72, 125.52, 117.78 ppm.

(*E*)-1-Phenyl-2-(phenylthio)-1,3-butadiene (7e) was prepared on a 1.00-mmol scale from benzaldehyde in 80% yield with workup B: R_f 0.26 (2% ether/petroleum ether); IR (neat) 1581 (m), 1478 (m), 1440 (m), 918 (s), 739 (s), 697 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz), δ 7.42–7.19 (m, 10 H), 6.99 (b s, 1 H), 6.89 (ddd, J = 17, 10.5, 1 Hz, 1 H), 5.86 (b d, J = 17 Hz, 1 H), 5.34 (dt, J = 10.5, 1.5 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 300 MHz) δ 136.4 (s), 136.2 (d), 135.37 (s), 133.97 (s), 131.75 (d), 129.89 (d), 129.32 (d), 128.95 (d), 128.28 (d), 127.62 (d), 126.44 (d), 120.03 (t) ppm; MS *m/e* (rel intensity) 241 (M^+ + 3, 0.4), 240 (M^+ + 2, 3), 239 (M^+ + 1, 10), 238 (M^+, 53), 223 (3), 205 (7), 167 (11), 147 (11), 129 (100), 102 (15), 77 (39), 51 (43); HMRS calcd for $C_{16}H_{14}S$ 238.0816, found 238.0808. Anal. Calcd for $C_{16}H_{14}S$: C, 80.64; H, 5.88. Found: C, 80.74; H, 6.20.

(*Z*)-5-Phenyl-3-(phenylthio)-1,3-pentadiene (6f) was prepared on a 0.50-mmol scale from phenylacetaldehyde in 68% yield: R_f 0.26 (2% ether/petroleum ether); IR (neat) 1584 (s), 1492 (s), 1478 (s), 1352 (s), 1438 (s), 1025 (s), 912 (s), 39 (s), 699 (s), 689 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.13–7.36 (m, 10 H), 6.43–6.53 (m, 2 H), 5.66 (dd, J = 17, 1 Hz, 1 H), 5.15 (b d, J = 10 Hz, 1 H), 3.87 (d, J = 7.5 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.17 (d), 139.58 (s), 136.94 (d), 136.35 (s), 132.36 (s), 128.89 (d), 128.65 (d), 127.40 (d)8 126.33 (d), 125.34 (d), 116.96 (t), 36.78 (t) ppm; MS *m/e* (rel intensity): 255 (M^+ + 3, 0.5), 254 (M^+ + 2, 4), 253 (M^+ + 1, 12), 252 (M^+, 60), 173 (9), 161 (22), 143 (93), 128 (100), 115 (74), 109 (15), 91 (19), 77 (27), 65 (73), 51 (48), 39 (67); HRMS calcd for $C_{17}H_{16}S$ 252.0973, found 252.0961.

(*E*)-5-Phenyl-3-(phenylthio)-1,3-pentadiene (7f) was prepared on a 0.50-mmol scale from phenylacetaldehyde in 84% yield:

R_f 0.26 (2% ether/petroleum ether); IR (neat) 1583 (s), 1494 (s), 1479 (s), 1452 (s) 1439 (s), 1025 (s), 920 (s), 738 (s), 697 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.17–7.40 (m, 10 H), 6.87 (ddd, J = 16.8, 10.6, 1 Hz, 1 H), 6.38 (b t, J = 7.8 Hz, 1 H), 5.81 (b d, J = 16.8 Hz, 1 H), 5.35 (dt, J = 10.6, 1 Hz, 1 H), 3.73 (d, J = 7.8 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.58, 139.32, 136.39, 131.62, 130.26, 128.82, 128.67, 128.55, 128.44, 126.40, 125.84, 119.56, 35.05 ppm; MS m/e (rel intensity) 255 (M^+ + 3, 1), 254 (M^+ + 2, 7), 253 (M^+ + 1, 20), 252 (M^+, 100), 161 (10), 141 (40), 128 (33), 115 (21), 91 (23), 65 (13); HRMS calcd for $C_{17}H_{16}S$ 252.0973, found 252.0962.

(*Z*)-8-Bromo-3-(phenylthio)-1,3-octadiene (6g) was prepared on a 0.80-mmol scale from 5-bromopentanal[20] in 73% yield: R_f 0.32 (2% ether/petroleum ether); IR (neat) 1623 (m), 1584 (s), 1478 (s), 1439 (s), 1250 (s), 1025 (s), 911 (s)8 739 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.09–7.27 (m, 5 H), 6.44 (dd, J = 16.5, 10.5 Hz, 1 H), 6.30, (t, J = 7 Hz, 1 H), 5.59 (dd, J = 16.5, 0.5 Hz, 1 H), 5.09 (dd, J = 10.5, 0.5 Hz, 1 H), 3.40 (t, J = 6.7 Hz, 2 H), 2.52 (q, J = 7.4 Hz, 2 H), 1.82–1.93 (m, 2 H), 1.54–1.65 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.07 (d), 136.86 (d), 136.31 (s), 132.40 (s), 128.72 (d), 127.07 (d), 125.10 (d), 116.32 (t), 33.37 (t), 32.22 (t), 29.36 (t), 27.46 (t) ppm; MS m/e (rel intensity) 301 (0.5), 300 (3), 299 (10), 298 (62), 297 (11), 296 (60), 217 (10), 175 (100), 161 (63), 147 (37), 142 (36), 123 (15), 110 (39), 107 (36), 97 (22), 91 (45), 79 (52), 77 (36); HRMS calcd for $C_{14}H_{17}{}^{79}BrS$ 296.0234, found 296.0226.

(*E*)-8-Bromo-3-(phenylthio)-1,3-octadiene (7g) was prepared on a 0.80-mmol scale from 5-bromopentanal[20] in 82% yield: R_f 0.23 (2% ether/petroleum ether); IR (neat) 1621 (w), 1583 (s), 1479 (s), 1439 (s), 1250 (s), 978 (s)8 917 (s), 740 (vs), 665 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.10–7.32 (m, 5 H), 6.70 (ddd, J = 16.7, 10.6, 0.9 Hz, 1 H), 6.18 (tt, J = 7.7, 0.9, 1 H), 5.70 (b d, J = 16.7 Hz, 1 H), 5.25 (dt, J = 10.6, 1.5 Hz, 1 H), 3.43 (t, J = 6.7 Hz, 2 H), 2.39 (q, J = 7.5 Hz, 2 H), 1.88–1.97 (m, 2 H), 1.58–1.70 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.01 (d), 136.49 (s), 131.37 (s), 130.16 (d), 128.72 (d), 128.31 (d), 125.65 (d), 118.92 (t), 33.18 (t), 32.18 (t), 28.04 (t), 27.74 (t) ppm; MS m/e (rel intensity) 301 (0.3), 300 (4), 200 (12), 298 (77), 297 (15), 296 (78), 221 (23), 219 (24), 193 (30), 191 (31), 175 (28), 161 (18), 110 (58), 107 (56), 93 (50), 91 (65), 79 (100); HRMS calcd for $C_{14}H_{17}{}^{79}BrS$ 296.0234, found 296.0234. Anal. Calcd for $C_{14}H_{17}BrS$: C, 56.39; H, 5.75. Found: C, 56.51; H, 5.84.

(*Z*)-7-Bromo-3-(phenylthio)-1,3-heptadiene (6h) was prepared on a 0.50-mmol scale from 4-bromobutanal[20] in 78% yield: R_f (0.29 (2% ether/petroleum ether); IR (NaCl, film) 1623 (w), 1584 (s), 1478 (s), 1437 (s), 1025 (s), 913 (s), 739 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.10–7.28 (m, 5 H), 6.44 (dd, J = 17, 10.5 Hz, 1 H), 6.29 (t, J = 7.4 Hz, 1 H), 5.60 (b d, J = 17 Hz, 1 H), 5.11 (b d, J = 10.5 Hz, 1 H), 3.40 (t, J = 6.8 Hz, 2 H), 2.64 (q, J = 7.4 Hz, 2 H), 1.95–2.05 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.17 (d), 136.72 (d), 136.17 (s), 133.22 (s), 128.77 (d), 127.18 (d), 125.22 (d), 116.70 (t), 32.79 (t), 32.08 (t), 29.04 (t) ppm; MS m/e (rel intensity) 286 (3), 285 (11), 284 (76), 283 (13), 282 (76), 175 (100), 147 (47), 110 (55), 97 (36), 91 (89), 77 (81), 65 (76), 41 (54); HRMS calcd for $C_{13}H_{15}{}^{79}BrS$ 282.0078, found 282.0078.

(*E*)-7-Bromo-3-(phenylthio)-1,3-heptadiene (7h) was prepared on a 0.50-mmol scale from 4-bromobutanal[20] in 86% yield: R_f 0.22 (2% ether/petroleum ether); IR (neat) 1583 (s), 1479 (s), 1439 (s), 1024 (s), 919 (s), 740 (s), 690 (s), 664 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.11–7.29 (m, 5 H), 6.73 (ddd, J = 17, 10.5, 1 Hz, 1 H), 6.11 (tt, J = 7.8, 0.8 Hz, 1 H), 5.71 (b d, J = 17 Hz, 1 H), 5.26 (dt, J = 10.5, 1.5 Hz, 1 H), 3.44 (t, J = 6.5 Hz, 2 H), 2.51 (q, J = 7.5 Hz, 2 H), 1.98–2.07 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.22 (d), 136.31 (s), 132.33 (s), 130.09 (d), 128.78 (d), 128.43 (d), 125.78 (d), 119.27 (t), 32.81 (t), 32.06 (t), 27.38 (t) ppm; MS m/e (rel intensity) 286 (3), 285 (10), 284 (69), 283 (13), 282 (70), 203 (21), 175 (64), 161 (56), 147 (29), 110 (69), 93 (100), 77 (87), 65 (54); HRMS calcd for $C_{13}H_{15}{}^{79}BrS$: 282.0078. Found: 282.0076.

5-Azidopentanal. A solution of tetrahydropyran (17.6 g, 0.20 mol) in dichloromethane (30 mL) was added dropwise over 20 min to an ice-cooled solution of boron tribromide (16.7 g, 6.6 mL, 0.067 mol,) in dichloromethane (50 mL). After the addition was complete, the ice bath was removed, and the reaction mixture was allowed to stir for 1 h at room temperature. A suspension of pyridinium chlorochromate (48 g, 0.22 mol) and alumina (18 g) in dichloromethane (150 mL) was next added over a period of 20 min. The reaction mixture was allowed to stir for an additional 0.5 h. It was then diluted with petroleum ether (200 mL), filtered through a Celite plug, and concentrated in vacuo to yield 28.9 g (84.7%) of a crude yellow oil. The crude bromoaldehyde and sodium azide (35.5 g, 0.53 M) were mixed in dimethyl sulfoxide (300 mL) and stirred at room temperature for 14 h. The reaction mixture was diluted with water (1 L) and extracted with five 150-mL portions of ether/petroleum ether (1:1). The organic phase was dried over sodium sulfate and concentrated in vacuo to yield 14.1 g of a crude yellow oil, which was purified by a bulb-to-bulb distillation, bp 60 °C air bath (2 mmHg), to give 8.9 g (33% overall from tetrahydropyran) of the title compound: IR (neat) 2095 (s), 1724 (s), 1679 (w), 1455 (m), 1267 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.81 (t, J = 1.3 Hz, 1 H), 3.26 (t, J = 6.3 Hz, 2 H), 2.45 (dt, J = 6.3, 1.3 Hz, 2 H), 1.55–1.75 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.62 (d), 51.08 (t), 43.16 (t), 28.25 (t), 19.21 (t) ppm; MS (CI, NH_3) m/e (rel intensity) 145 ($M^+ + NH_4^+$, 5), 128 (MH^+, 7.9), 101 (8.7), 100 (100), 84 (8.6), 82 (7.0); HRMS calcd for $C_5H_9N_3OH^+$ 128.0824, found 128.0824.

(*Z*)-8-Azido-3-(phenylthio)-1,3-octadiene (6i) was prepared on a 1.00-mmol scale from 5-azidopentanal in 79% yield: R_f 0.16 (2% ether/petroleum ether); IR (neat) 2096 (s), 1583 (w), 1478 (m), 740 (m), 690 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.09–7.29 (m, 5 H), 6.43 (dd, J = 16.8, 10.5 Hz, 1 H), 6.29 (t, J = 7.3 Hz, 1 H), 5.56 (b d, J = 16.8 Hz, 1 H), 5.08 (b d, J = 10.5 Hz, 1 H), 3.25 (t, J = 6.8 Hz, 2 H), 2.50 (q, J = 7 Hz, 2 H), 1.51–1.68 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.22 (d), 146.91 (d), 136.39 (s), 132.44 (s), 128.79 (d), 127.09 (d), 125.16 (d), 116.40 (t), 51.15 (t), 29.71 (t), 28.42 (t), 26.06 (t) ppm; MS (CI/NH_3) m/e (rel intensity) 278 (MNH_4^+ + 1, 2), 277 (MNH_4^+, + 14), 232 (100), 136 (9), 123 (32), 109 (3), 93 (3); HRMS calcd for $C_{14}H_{17}SN_3NH_4$ 277.1487, found 277.1490.

(*E*)-8-Azido-3-(phenylthio)-1,3-octadiene (7i) was prepared on a 1.00-mmol scale from 5-azidopentanal in 86% yield: R_f 0.13 (2% ether/petroleum ether); IR (neat) 2096 (s), 1583 (w), 1479 (m), 740 (m), 690 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.10–7.28 (m, 5 H), 6.69 (ddd, J = 17, 10.5, 1 Hz, 1 H), 6.16 (b t, J = 8 Hz, 1 H), 5.69 (b d, J = 17 Hz, 1 H), 5.24 (dt, J = 10.5, 1.5 Hz, 1 H), 3.30 (t, J = 6.5 Hz, 2 H), 2.39 (q, J = 7.5 Hz, 2 H), 1.51–1.71 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.16, 136.48, 131.28, 130.11, 128.74, 128.25, 125.66, 118.96, 51.22, 28.43, 26.39 ppm; MS m/e (rel intensity) 259 (M^+, 0.6), 258 (4), 230 (22), 198 (37), 160 (42), 122 (40), 109 (42), 91 (56), 71 (50), 51 (43), 41 (100); HRMS calcd for $C_{14}H_{17}SN_3NH_4$ 277.1487, found 277.1490.

(*Z*)-7-Azido-3-(phenylthio)-1,3-heptadiene (6j) was prepared on a 2.50-mmol scale from 4-azidobutanal[21] in 63% yield. R_f 0.2 (2% ethyl acetate/hexane); IR (neat) 2094 (s), 1622 (w), 1583 (m), 1477 (m), 1438 (m), 739 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.1–7.4 (m, 5 H), 6.43 (dd, J = 17, 10.6 Hz, 1 H), 6.28 (t, J = 7.4 Hz, 1 H), 5.58 (b d, J = 17 Hz, 1 H), 5.1 (b d, J = 10.6 Hz, 1 H), 3.26 (t, J = 6.9 Hz, 2 H), 2.55 (q, J = 7.4 Hz, 2 H), 1.64–1.71 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.72, 136.96, 136.34, 133.39, 128.88, 127.43, 125.38, 116.70, 51.03, 28.30, 27.62 ppm; MS (CI/NH_3) m/e (rel intensity) 217 (M − 28, 4), 216 (11), 146 (77), 115 (33), 91 (27), 80 (100), 77 (56), 71 (50). Anal. Calcd for $C_{13}H_{15}N_3S$: C, 63.64; H, 6.17; N, 17.14. Found: C, 63.62; H, 6.27; N, 17.04.

(*E*)-7-Azido-3-(phenylthio)-1,3-heptadiene (7j) was prepared on a 2.50-mmol scale from 4-azidobutanal[21] in 80% yield: R_f 0.18 (2% ethyl acetate/hexane); IR (neat) 2096 (s), 1620 (w), 1582 (m), 1478 (m), 1439 (m), 740 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.10–7.40 (m, 5 H), 6.70 (ddd, J = 16.7, 10.6, 1 Hz, 1 H), 6.12 (b t, J = 7.4 Hz, 1 H), 5.70 (b d, J = 16.7 Hz, 1 H), 5.25 (dt, J = 10.6, 1.0 Hz, 1 H), 3.33 (t, J = 6.7 Hz, 2 H), 2.43 (q, J = 7.4 Hz, 2 H), 1.80–1.67 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.34, 136.31, 132.32, 130.08, 128.80, 128.63, 125.86, 119.27, 50.79, 28.48, 26.05 ppm; MS m/e (rel intensity) 217 (M − 28, 3), 216 (12), 202 (4), 184 (11), 146 (78), 115 (38), 91 (28), 80 (100), 65 (53). Anal. Calcd for $C_{13}H_{15}N_3S$: C, 63.64; H, 6.17; N, 17.14. Found: C, 63.77; H, 6.13; N, 17.37.

(1*E*,3*Z*)-1-Phenyl-4-(phenylthio)-1,3,5-hexatriene (6k) was prepared on a 0.50-mmol scale from *trans*-cinnamaldehyde in 66% yield. The triene was found to be unstable and polymerized on standing at room temperature and was not fully characterized: R_f 0.25 (1% ether/petroleum ether); ^1H NMR ($CDCl_3$, 300 MHz)

δ 7.59 (dd, J = 16.5, 11 Hz, 1 H), 7.10–7.53 (m, 9 H), 6.94 (b d, J = 10.05 Hz, 1 H), 6.81 (b d, J = 16.5 Hz, 1 H), 6.54 (ddd, J = 16.5, 10.5, 1 Hz, 1 H), 5.70 (b d, J = 16.5 Hz, 1 H), 5.17 (d, J = 10.5 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.68 (d) 137.09 (d), 136.95 (s), 136.80 (d), 136.44 (s), 132.15 (s), 128.83 (d), 128.63 (d), 128.25 (d), 127.46 (d), 126.91 (d), 126.21 (d), 125.39 (d), 117.48 (t) ppm.

(1*E*,3*E*)-1-Phenyl-4-(phenylthio)-1,3,5-hexatriene (7k) was prepared on a 0.50-mmol scale from *trans*-cinnamaldehyde in 83% yield. The triene was found to be unstable and polymerized on standing at room temperature and was not fully characterized: R_f 0.25 (1% ether/petroleum ether); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.18–7.46 (m, 11 H), 6.99 (dd, J = 16.5, 10.5 Hz, 1 H), 6.58–6.98 (m, 2 H), 7.75 (d, J = 16.5 Hz, 1 H), 5.33 (dt, J = 10.5, 1.5 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.87 (s), 136.48 (d), 135.50 (s), 135.16 (d), 132.72 (s), 130.53 (d), 129.70 (d), 128.90 (d), 128.65 (d), 128.09 (d), 126.67 (d), 126.34 (d), 123.30 (d), 118.99 (t) ppm.

Reaction of Aldehyde (8) with Allylborane (4). Preparation of (*E*)-5-Acetoxy-8-azido-3-(phenylthio)-1,3-octadiene (9). To the allene **3** (260 mg of 94% pure material, 3.9 mmol, neat) was added 9-BBN (7.8 mL of 0.5 M solution in THF, 3.9 mmol). After stirring at 35 °C for 2 h, the mixture was cooled to 25 °C, and a solution of 2-acetoxy-5-azidopentanal (**8**)[22] (650 mg, 3.5 mmol) in THF (1 mL) was added slowly. After 2 h, 4 N sodium hydroxide (10 drops) was added, and stirring was continued for another 2 h. A small aliquot (ca. 0.2 mL) was removed, and the solvent was evaporated. ^{1}H NMR spectroscopy showed only the *E* isomer of **9** to the limits of detection of our 300-MHz instrument. The reaction mixture was then diluted with pentane (8 mL) and washed with brine (3 × 3 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo, and the residue was purified by flash chromatography (30:1 hexane/ethyl acetate) to give 1.04 g (93%) of **9**, which was found to be a >97:<3 ratio of *E* and *Z* isomers: R_f 0.54 (5/1 hexane/ethyl acetate); IR (neat) 2096 (s), 1738 (s), 1624 (w), 1582 (s), 1479 (m), 1439 (m), 1370 (s), 1235 (br) 1023 (m), 925 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.16 (m, 5 H), 6.79 (dd, J = 16.9, 10.6 Hz, 1 H), 5.76 (dd, J = 16.9, 1.2 Hz, 1 H), 5.71–5.68 (m, 2 H), 5.35 (dd, J = 10.6, 1.2 Hz, 1 H), 3.29 (t, J = 6.7 Hz, 2 H), 2.05 (s, 3 H), 1.82–1.53 (m, 4 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.07 (s), 136.50 (s), 134.33 (s), 133.24 (d), 130.56 (d), 130.23 (d), 129.02 (d), 126.84 (d), 120.63 (t), 69.76 (d), 51.03 (t), 31.79 (t), 24.57 (t), 21.04 (q) ppm; MS *m/e* (rel intensity) 289 (0.3), 230 (18), 191 (5), 178 (12), 120 (30), 109 (11), 91 (15), 77 (14), 43 (100); HRMS (CI) calcd for $C_{16}H_{20}NO_2S$ ($MH^+ - N_2$) 290.1215, found 290.1218.

Reaction of Aldehyde (8) with Allyltitanium Reagent (1). The procedure by Yamamoto[4b] was followed exactly. To a solution of 1-(phenylthio)-1-(trimethylsilyl)-2-propene (223 mg, 1.0 mmol) in THF (2.5 mL) was added *n*-butyllithium (0.45 mL of 2.24 M solution in hexanes, 1.0 mmol) at 0 °C. After being stirred for 1 h, the solution was cooled to −78 °C, and titanium isopropoxide (0.30 mL, 280 mg, 1.0 mmol) was added. After 10 min, the mixture was warmed to 0 °C, stirred for 1 h to complete the formation of reagent **1**, and recooled to −78 °C. The aldehyde **8**[22] (158 mg, 0.85 mmol) in THF (0.5 mL) was then added, and the solution was stirred for 10 min at −78 °C, 1 h at 0 °C, and 1 h at room temperature. The mixture was poured into 2 N HCl and extracted with ether. The organic layer was dried (Na_2SO_4) and concentrated. Flash chromatography of the residue (gradient elution from 1:50 to 1:5 ethyl acetate/hexane) gave 79 mg (29%) of **9** (R_f 0.54 in 1:5 ethyl acetate/hexane), 52 mg (22%) of **10** (R_f 0.26 in 1:5 ethyl acetate/hexane), and 68 mg (22%) of **11** (R_f 0.12 in 1:5 ethyl acetate/hexane). Diene **9** proved to be an inseparable 95:5 *E*:*Z* mixture by ^{1}H NMR spectroscopy.

For **10**: NMR of the purified product showed an 85:15 ratio of *E*:*Z* isomers. Data for *E* isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38–7.26 (m, 5 H), 6.67 (dd, J = 16.8, 10.7 Hz, 1 H), 5.80 (d, J = 8.8 Hz, 1 H), 5.74 (dd, J = 16.8, 1.1 Hz, 1 H), 5.32 (dd, J = 10.6, 1.1 Hz, 1 H), 4.70–4.61 (m, 1 H), 3.31 (t, J = 6.2 Hz, 2 H), 1.76–1.54 (m, 5 H) ppm; MS *m/e* (rel intensity) 247 (8), 228 (9), 190 (16), 160 (37), 147 (25), 110 (56), 91 (57), 77 (63), 71 (77), 65 (45), 53 (100), 43 (72); HRMS (EI) calcd for $C_{14}H_{17}NOS$ ($M^+ - N_2$) 247.1031, found 247.1030.

For **11** (NMR showed a mixture of several stereoisomers, which were not separated): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35–7.10 (m, 5 H), 6.68 (t, J = 6.7 Hz, 1 H), 3.73–3.58 (m, 1 H), 3.57–3.38 (m, 1 H), 3.29 (t, J = 7.7 Hz, 2 H), 2.64 (m, 2 H), 1.90–1.38 (m, 4 H) ppm; MS *m/e* (rel intensity) 365 (4), 222 (6), 167 (19), 151 (9), 149 (10), 109 (5), 91 (7), 73 (100), 43 (17); HRMS (EI) calcd for $C_{17}H_{27}N_3O_2SSi$ (M^+) 365.1593, found 365.1580.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for all new compounds which do not have elemental analyses (43 pages). Ordering information is given on any current masthead page.

The Reaction of Sodium *N*-Methylbenzohydroxamate with Sanger's Reagent and the Unusual Mass Spectrum of the Product

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Current interest in the chemistry of *N*-methylbenzohydroxamic acids (NMBHAH) includes examples of alkylation with methyl groups on both the carbonyl O[1] or thiocarbonyl[2] and on the hydroxamate O.[3] The exact nature of the reaction conditions, whether the acid is present as the acid or its salt, determines the position of alkylation. Our interest in these species as potential single electron transfer nucleophiles (SET) in nucleophilic aromatic substitution[4] and α-nucleophiles[5,6] prompts us to report in this paper the reactivity of the sodium salt of *p*-ClNMBHAH with 2,4-dinitrofluorobenzene (Sanger's reagent). The chemical behavior of this system is previously not reported, and it is not clear from elementary considerations where an activated aromatic system should attach.

The Na *p*-ClNMBHA was prepared by addition of an equivalent amount of NaOMe in MeOH to freshly pre-

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