= 5.9 Hz, 2 H), 1.52 (dt, J = 11.0, 3.6 Hz, 1 H); UV (cyclohexane) λ_{max} = 274 (12.0), 283 (13.4), 295 nm (sh, 11); MS (25 eV) m/z (relative intensity) 172 (M^+, 9), 129 (16), 128 (16), 107 (100), 79 (25), 78 (17), 66 (45).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.52; H, 6.83.

The 2D NOESY spectrum for **20** showed a cross peak between H_3 (H_6) (3.34 ppm) and one of the methylene protons at C_{11} (2.49 ppm).

Photolysis of Quadricyclanone (2) in Furan. A solution of quadricyclanone (**2**, 211.2 mg, 1.99 mmol) in 130 mL of furan in quartz vessel was irradiated with 4 RUL-3000Å lamps for 20 h under N_2. Removal of furan in vacuo gave 451 mg of a yellow oil. After passing the material through a short column of silica gel (33% ethyl acetate in *n*-hexane), a crude photolysate was separated by MPLC on silica gel (column A). Elutions with 9% ethyl acetate in *n*-hexane and with 17% ethyl acetate in *n*-hexane afforded **2** (8.9 mg, 4%) and **22** (172.4 mg, 50%) as pale yellow crystals which was recyrstallized from *n*-hexane to give colorless plates.

22: mp 81-81.5 °C; IR (KBr) 1751, 1130, 1010, 741, 702 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.36 (s, 2 H), 6.00 (s, 2 H), 4.80 (d, J = 3.6 Hz, 2 H), 3.55 (s, 2 H), 2.51 (d, J = 3.6 Hz, 2 H); UV (cyclohexane) λ_{max} = 274 (11.4), 283 (12.9), 293 (sh, 11.2), 307 nm (sh, 6.0); MS (25 eV) m/z (relative intensity) 174 (M^+, 3), 146 (69), 145 (100), 131 (31), 117 (76), 115 (31), 91 (35), 81 (31), 78 (55), 68 (69).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.78; H, 5.86.

Photolysis of Quadricyclanone (2) in Methanol. A solution of quadricyclanone (**2**, 303.1 mg, 2.86 mmol) in 700 mL of methanol was irradiated with 4 RUL-3000Å lamps for 6 h under N_2. Removal of methanol in vacuo gave 297 mg of a yellow oil, which was chromatographed on silica gel (50 g). Elution with 14% ether in *n*-pentane gave 39.4 mg of exo adduct **23** (10%) as a pale yellow oil and 72.4 mg of recovered **2** (24%). Elutions with 14% ether in *n*-pentane and 33% ether in *n*-pentane gave 55.3 mg of endo adduct **24** (14%) as a pale yellow oil. **23** and **24** were further purified as a colorless oil by distillation.

23: bp 64-73 °C (35 mmHg); IR (neat) 2816, 1747, 1090, 1068, 784, 740 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 6.16 (d, J = 2.7 Hz, 1 H), 5.98 (br d, J = 2.7 Hz, 1 H), 3.47 (dd, J = 8.5, 3.5 Hz, 1 H), 3.39 (s, 3 H), 3.35 (d, J = 3.5 Hz, 1 H), 3.24 (s, 1 H), 2.66 (dd, J = 17.5, 8.5 Hz, 1 H), 2.19 (d, J = 17.5 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 214.15, 143.03, 135.37, 82.33, 57.65, 49.49, 41.99, 39.40; HRMS (M^+) calcd for $C_8H_{10}O_2$ 138.0681, obsd 138.0675.

24: bp 65-75 °C (22 mmHg); IR (neat) 2816, 1753, 1135, 1110-1098 (br), 776 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.17 (br d, J = 2.9 Hz, 1 H), 6.14 (br d, J = 2.9 Hz, 1H), 4.09 (dd, J = 8.3, 2.1 Hz, 1 H), 3.66 (dd, J = 8.3, 3.7 Hz, 1 H), 3.54 (s, 3 H), 3.44 (ddd, J = 8.2, 3.7, 0.9 Hz, 1 H), 2.50 (ddd, J = 17.1, 8.2, 2.1 Hz, 1 H), 2.22 (dd, J = 17.1, 0.9 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 211.80, 141.13, 136.97, 84.74, 58.32, 43.95, 39.02, 37.78; HRMS (M^+) calcd for $C_8H_{10}O_2$ 138.0681, obsd 138.0677.

Stereoselective Synthesis of Terminal 1,3-Butadienes by the Condensation Reaction of Aldehydes and Ketones with the γ-Trimethylsilyl-Substituted Allylboranes

Kung K. Wang,* Chin Liu, Yu Gui Gu, and Friedrich N. Burnett

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

Prem D. Sattsangi

Department of Chemistry, The Pennsylvania State University, Fayette Campus, Uniontown, Pennsylvania 15401

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Allylboranes **7-12**, readily prepared from allenylsilanes **1-6** by hydroboration with 9-borabicyclo[3.3.1]nonane, smoothly condense with aldehydes and ketones to afford, after basic or acidic workup to promote the Peterson olefination reaction, a variety of terminal 1,3-butadienes. The dienes derived from aldehydes have high isomeric purity except in the cases with allylborane **12**. Apparently, high diastereoselectivity was obtained during the condensation step with **7-11** to form **14**. In each case, by simply changing the workup conditions to induce syn or anti elimination of hydroxytrimethylsilane, either the Z or the E isomer of the diene was obtained.

The synthetic utility of 1,3-butadienes in the Diels-Alder reaction[1] and the discovery of many biologically active natural products possessing a conjugated diene functionality[2] have prompted the development of a large number of stereoselective synthetic methods for the preparation of these compounds.[3] We recently reported a simple and stereoselective route to 2-[(trimethylsilyl)methyl]-1,3-butadienes using 1,2-bis(trimethylsilyl)-2,3-butadiene (**3**) as the starting material (Scheme I).[3a] The ready availability of a variety of trimethylsilyl-substituted terminal allenes[4] allows the extension of this methodology to the synthesis of many other terminal 1,3-butadienes.[5] We now disclose the full account of the research effort in this area.

Hydroboration of allenes **1-6** with 9-borabicyclo-[3.3.1]nonane[6] afforded the corresponding allylboranes **7-12** (Scheme I). Allylboranes **7-11** had predominantly the E geometry (E:Z ≥ 91:9), whereas allylborane **12**

(1) Ciganek, E. *Org. React. (N.Y.)* **1984**, *32*, 1-374 and referenced cited therein.

(2) (a) Henrick, C. A. *Tetrahedron* **1977**, *33*, 1845-1889. (b) Rossi, R. *Synthesis* **1977**, 817-836.

(3) (a) Liu, C.; Wang, K. K. *J. Org. Chem.* **1986**, *51*, 4733-4734. (b) Wang, K. K.; Gu, Y. G.; Liu, C. *J. Am. Chem. Soc.* **1990**, *112*, 4424-4431 and references cited therein. (c) Pearson, W. H.; Lin, K.-C.; Poon, Y.-F. *J. Org. Chem.* **1989**, *54*, 5814-5819. (d) Tsai, D. J. S.; Matteson, D. S. *Tetrahedron Lett.* **1981**, *22*, 2751-2752. (e) Yamamoto, Y.; Saito, Y.; Maruyama, K. *J. Organomet. Chem.* **1985**, *292*, 311-318. (f) Ikeda, Y.; Ukai, J.; Ikeda, N.; Yamamoto, H. *Tetrahedron* **1987**, *43*, 723-730, 731-741 and references cited therein. (g) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033-3040 and references cited therein. (h) Björling, F.; Norin, T.; Unelius, C. R.; Miller, R. B. *J. Org. Chem.* **1987**, *52*, 292-294. (i) Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972-980. (j) Block, E.; Aslam, M.; Eswarakrishnan, V.; Gebreyes, K.; Hutchinson, J.; Iyer, R.; Laffitte, J.-A.; Wall, A. *J. Am. Chem. Soc.* **1986**, *108*, 4568-4580.

(4) (a) Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390-392. (b) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935-947. (c) Danheiser, R. L.; Tsai, Y.-M.; Fin, D. M. *Org. Synth.* **1987**, *66*, 1-7. (d) Montury, M.; Psaume, B.; Gore, J. *Tetrahedron Lett.* **1980**, *21*, 163-166.

(5) See ref 3b for the stereoselective synthesis of all four geometric isomers of internal 1,3-butadienes from aldehydes with γ-trimethylsilyl-substituted allylboranes.

(6) (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.

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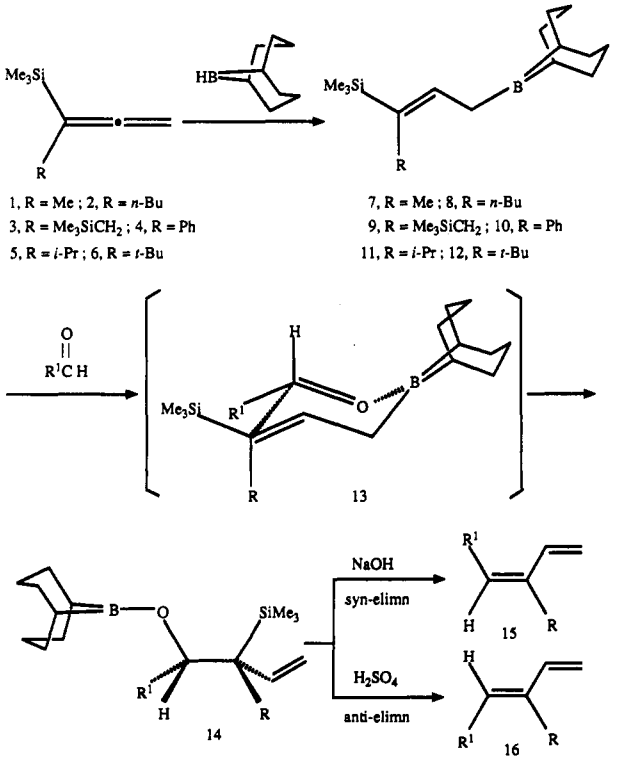
Table I. Stereoselective Synthesis of Terminal 1,3-Butadienes

diene	workup (time)	R	R^1	isolated yield, %	isomer ratio,[a] 15:16
15a	NaOH (2 h)	Me	n-C_5H_{11}	73	95:5
15a	NaOEt (30 min)			72	98:2
16a	H_2SO_4 (1 h)			65	3:97
15b	NaOH (40 min)	Me	Ph	71	98:2
16b	H_2SO_4 (2 h)			69	2:98
15c	NaOH (2 h)	n-Bu	n-C_5H_{11}	81	96:4
16c	H_2SO_4 (2 h)			70	3:97
15d	NaOH (1 h)	n-Bu	Ph	81	98:2
16d	H_2SO_4 (2 h)			75	2:98
15e	NaOH (2 h)	n-bu	(E)-CH_3CH=CH	53	93:7
15f	NaOH (30 min)	Me_3SiCH_2	Me	61	98:2
16f	H_2SO_4 (30 min)			50	2:98
15g	NaOH (30 min)	Me_3SiCH_2	n-C_5H_{11}	82	97:3
15g	NaOEt (30 min)			85	97:3
16g	H_2SO_4 (30 min)			87	0.5:99.5
15h	NaOH (30 min)	Me_3SiCH_2	Ph	88	98:2
16h	H_2SO_4 (40 min)			83	2:98
15i	NaOH (2 h)	Me_3SiCH_2	(E)-CH_3CH=CH	59	98:2
15j	NaOH (30 min)	Ph	n-C_5H_{11}	67	96:4
15j	NaOEt (15 min)			80	95:5
16j	H_2SO_4 (2 h)			84	5:95
15k	NaOH (15 min)	Ph	Ph	58	>99.5:0.5
16k	H_2SO_4 (2 h)			56	<0.5:99.5
15l	NaOH (30 min)	i-Pr	n-C_5H_{11}	77	88:12
15l	NaOEt (30 min)			82	88:12
16l	H_2SO_4 (2 h)			65	11:89
15m	NaOH (30 min)	i-Pr	Ph	85	91:9
16m	H_2SO_4 (2 h)			84	11:89
15n	NaOH (2 h)	t-Bu	n-C_5H_{11}	55	41:59
15n	NaOEt (1 h)			79	29:71
16n	H_2SO_4 (5 h)			69	72:28
15o	NaOH (30 min)	t-Bu	Ph	70	41:59
15o	NaOEt (30 min)			83	29:71
16o	H_2SO_4 (1.5 h)			68	62:38

[a] The isomer ratio was determined by the integration of the 270-MHz ^1H NMR spectrum. The detection level for the minor isomer is estimated to be 0.5%.

Scheme I



slightly favored the Z isomer (E:Z = 28:72). Subsequent condensation of these allylboranes with hexanal, benzaldehyde, acetaldehyde, or crotonaldehyde proceeded smoothly and afforded the corresponding 1,3-butadienes after either basic or acidic workup (Table I).

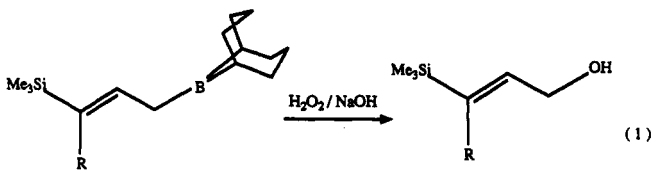
Table II. The Geometry of the Double Bond of Allylboranes 7–12

allylborane	E:Z ratio[a]	allylborane	E:Z ratio[a]
7	98:2 (>99:1)	10	99:1 (98:2)
8	97:3 (98:2)	11	91:9 (92:8)
9	97:3 (>99:1)	12	28:72 (42:58)

[a] Numbers in parentheses refer to the E:Z ratios of the corresponding allylic alcohols

The geometry of the double bonds in 7–12 (Table II) was assigned on the basis of their ^1H NMR spectra measured in tetrahydrofuran-d_8 (THF-d_8). In the case of **7**, a major triplet of quartets (98%) at δ 6.13 was attributed to the vinylic hydrogen of the E isomer, whereas a minor triplet at δ 6.32 was attributed to the vinylic hydrogen of the Z isomer (Figure 1). The assignment of the major signal at δ 6.13 to the E isomer is based on earlier reports that vinylic hydrogens cis to the trimethylsilyl group consistently exhibited ca. 0.3 ppm upfield shift with respect to the corresponding vinylic hydrogens trans to the trimethylsilyl group.[7] To further confirm the geometrical assignments, allylborane **7** was oxidized to the corresponding allylic alcohol **17** by alkaline H_2O_2 (eq 1). Again, the major isomer was found to have the E geometry (Table II) by comparing the ^1H NMR spectrum with the reported data.[8]

(7) Chan, T. H.; Mychajlowskij, W.; Amoroux, R. *Tetrahedron Lett.* 1977, 1605–1608.
(8) (a) Stork, G.; Jung, M. E.; Colvin, E.; Noel, Y. *J. Am. Chem. Soc.* 1974, *96*, 3684–3686. (b) Audia, J. E.; Marshall, J. A. *Synth. Commun.* 1983, *13*, 531–535. (c) Uchida, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* 1977, *33*, 2987–2992.



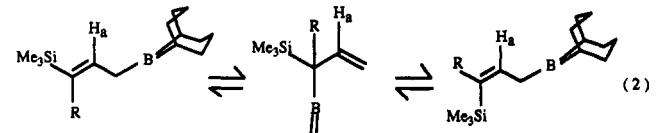
(1)

7, R = Me ; 8, R = *n*-Bu
9, R = Me_3SiCH_2 ; 10, R = Ph
11, R = *i*-Pr ; 12, R = *t*-Bu

17, R = Me ; 18, R = *n*-Bu
19, R = Me_3SiCH_2 ; 20, R = Ph
21, R = *i*-Pr ; 22, R = *t*-Bu

The *E* isomers were also the predominant species in the cases of 8–11 (Table II). However, a reversal of selectivity was observed in the case of 12. The geometry of these allylboranes was similarly assigned as in the case of 7 (Figure 1). The geometry of the allylic alcohol 18 was also determined by comparing its ^1H NMR spectrum with the reported data.[8c] The nuclear Overhauser effect was employed to confirm the almost exclusive formation of the *E* isomer of 19 from allylborane 9. The *Z* isomers of alcohols 20–22 were independently synthesized from the corresponding allylic alcohols 23–25 (Scheme II)[9] and their ^1H and ^{13}C NMR spectra were utilized to compare with those derived from oxidation of 10–12.

On surface, these results seem to suggest that hydroboration of 1–5 occurred preferentially from the side of the bulkier trimethylsilyl group[10] and in the case of 6 from the *tert*-butyl side, contradicting the general behavior of the hydroboration reaction which prefers the less hindered side of a carbon–carbon double bond.[11] However, since allylic boranes are known to undergo rapid [1,3] sigmatropic rearrangement which provides a pathway for interconverting the geometry of the double bond (eq 2),[6] it is possible that the product distribution summarized in Table II reflects only the thermodynamic equilibrium of the *E* and the *Z* isomers of allylboranes 7–12, rather than the kinetic preference of the hydroboration step.



(2)

7a, R = Me ; 8a, R = *n*-Bu
9a, R = Me_3SiCH_2 ; 10a, R = Ph
11a, R = *i*-Pr ; 12a, R = *t*-Bu

7b, R = Me ; 8b, R = *n*-Bu
9b, R = Me_3SiCH_2 ; 10b, R = Ph
11b, R = *i*-Pr ; 12b, R = *t*-Bu

Attempts were made to determine the rates of the [1,3] sigmatropic rearrangements of 7–12 by studying the dynamic behavior of the ^1H NMR. Irradiation of H_a of **7b** in THF-d_8 at δ 6.32 did not significantly diminish the intensity of H_a of **7a** at δ 6.13. Interestingly, when a magnetization transfer experiment was carried out in toluene-d_8, a 66% decrease in intensity of H_a of **7a** at δ 6.03 was observed on irradiation of H_a of **7b** at δ 6.30 (**7a**:**7b** = 98:2). The slower rate of exchange in THF-d_8 can be attributed to complexation of 7 with the solvent. Indeed, the ^{11}B NMR chemical shift of 7 in THF-d_8 is at δ 40,

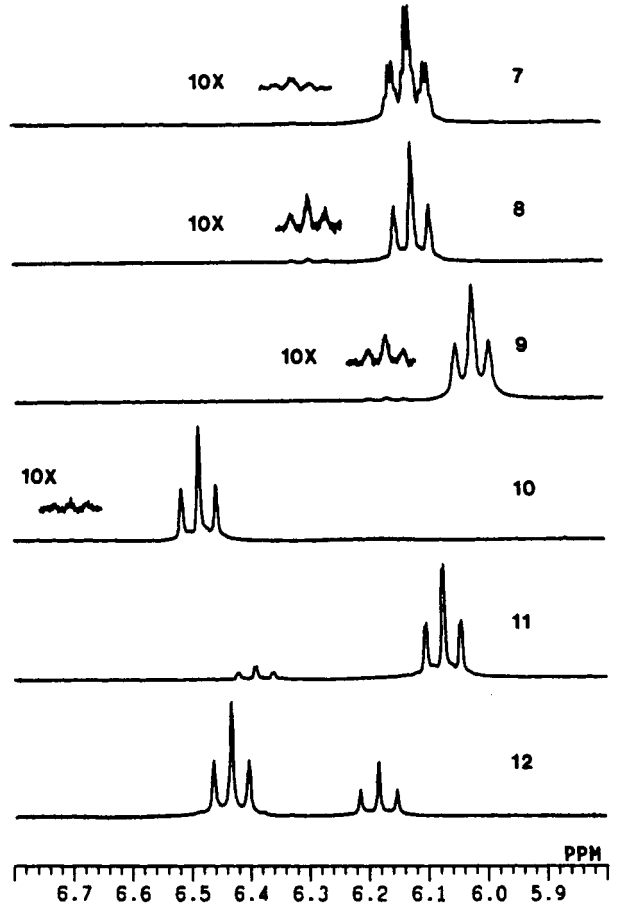
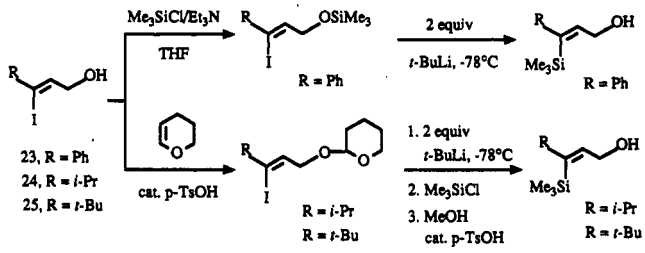


Figure 1. The vinylic hydrogen region of the ^1H NMR spectra of allylboranes 7–12.

Scheme II



indicating substantial complexation, whereas the ^{11}B NMR chemical shift of 7 in toluene-d_8 is at δ 84. Increasing the steric bulkiness of the R group from methyl to *tert*-butyl should result in decreased rate of exchange. Indeed, no magnetization transfer was observed for allylboranes 8–12 in THF-d_8. The ^{11}B NMR chemical shifts of 8–12 in THF-d_8 are at δ 49, 50, 34, 50, and 66, respectively, again showing significant complexation with the solvent.

Although the rates of these [1,3] sigmatropic rearrangements in THF are too slow to be measured by the ^1H NMR studies, it is possible that they are still faster than the rates of hydroboration of allenes 1–6, allowing complete equilibration between the two resulting geometrical isomers. The large $A^{(1,3)}$ allylic interaction[12] with the sterically bulkier trimethylsilyl group in **7b**–**11b** is probably responsible for shifting the equilibrium toward **7a**–**11a**. On the other hand, interaction with the *tert*-butyl group is more severe, and **12b** becomes the preferred isomer.

Dienes summarized in Table I have high isomeric purity except in the cases where R = *tert*-butyl. Apparently the

(9) (a) Denmark, S. E.; Jones, T. K. *J. Org. Chem.* **1982**, *47*, 4595–4597. (b) Marshall, J. A.; Shearer, B. G.; Crooks, S. L. *J. Org. Chem.* **1987**, *52*, 1236–1245. (c) The procedure using the intramolecular migration of the trimethylsilyl group was kindly shared with us by Professor Magriotis. Kim, K. D.; Magriotis, P. *Tetrahedron Lett* **1990**, *31*, 6137–6140. The use of tetrahydropyranyl ether as the protecting group for the synthesis of (*Z*)-3-(trimethylsilyl)-3-phenyl-2-propen-1-ol resulted in very low yield. This is presumably due to the high sensitivity of (*Z*)-3-(trimethylsilyl)-3-phenyl-2-propen-1-ol toward the acidic workup for deprotection. (d) See ref 3b for the procedure using tetrahydropyranyl ether as the protecting group.

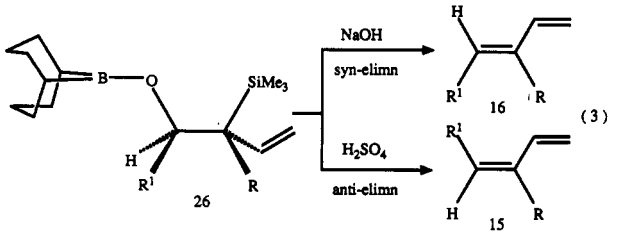
(10) (a) Kitching, W.; Olszowy, H. A.; Drew, G. M.; Adcock, W. *J. Org. Chem.* **1982**, *47*, 5153–5156. (b) Hwu, J. R.; Wang, N. *Chem. Rev.* **1989**, *89*, 1599–1615.

(11) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1959**, *81*, 247.

(12) Johnson, F. *Chem. Rev.* **1968**, *68*, 375–413.

condensation step is highly diastereoselective with 7–11, producing predominantly 14 (Scheme I). This is presumably due to the R^1 group of aldehydes preferentially adopting the equatorial position in the six-membered chair-type cyclic transition state 13 during condensation with the major isomers **7a–11a**. Reaction with the minor isomers **7b–11b** could also lead to 14 by having the R^1 group assuming the axial position. It is conceivable that the minor *Z* isomers **7b–11b** could also serve as important reacting species by the way of a rapid allylic rearrangement (eq 2) prior to condensation with aldehydes, although it was reported that in the case of crotyldiisopinocampheylborane the rate of condensation with aldehydes was faster than that of isomerization.[13] Subsequent treatment with NaOH or NaOEt to promote the Peterson olefination reaction[14] afforded dienes **15** as the major isomer after syn elimination of trimethylsilyl oxide. On the other hand, dienes **16** were obtained preferentially by using concentrated H_2SO_4 to induce anti elimination.[14]

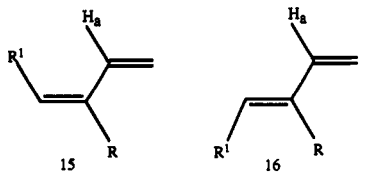
The minor diene isomers also could come from two sources. The adoption of the axial position by the R^1 group in 13 would produce **26**, which after syn elimination would afford dienes **16**, and after anti elimination would give diene **15** (eq 3). Condensation through the minor *Z* isomers **7b–11b** with the R^1 group remaining equatorial as shown in 13 would also lead to **26**, resulting in the formation of the minor diene isomers.



(3)

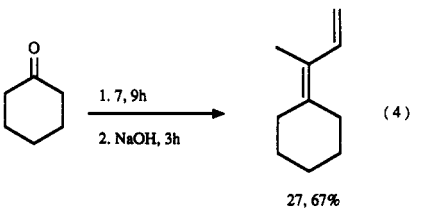
The close resemblance of the isomer ratios between the *E* and the *Z* isomers of allylborane **12** and the resulting dienes does not necessarily indicate that the R^1 group also prefers the equatorial position during condensation with **12a** and **12b**. Various combinations of different equatorial to axial ratios during condensation with **12a** and **12b** could also account for the observed diene isomer distributions.

The double-bond geometry of the dienes in Table I was determined by comparing the ^1H and ^{13}C NMR spectra of the known compounds with those of the reported data. The assignment of the geometry to dienes with R = Ph, isopropyl, or *tert*-butyl was based on their reactivities toward maleic anhydride. Dienes **16** exhibited very high reactivities at 50 °C in $CDCl_3$, whereas dienes **15** showed virtually no reactivity. The remaining dienes with R = *n*-butyl or Me_3SiCH_2 were assigned geometry on the basis of the ^1H NMR chemical shift correlation. The chemical shift of H_a in **15** is generally ca. 0.4 ppm downfield from that of **16**.[15] Such a difference of chemical shifts was also observed consistently with other dienes summarized in Table I except in the cases where R = *tert*-butyl.



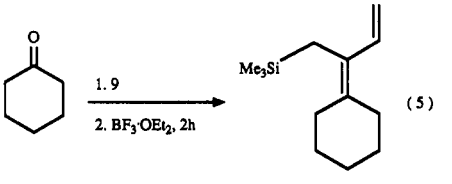
The Peterson olefination reaction induced by both NaOH and NaOEt is very facile. The elimination of trimethylsilyl oxide is essentially complete in less than 2 h. Interestingly, when an excess of 30% H_2O_2 was added immediately after the introduction of aqueous NaOH, the reaction rates of the Peterson olefination reaction were dramatically reduced in many cases, especially with intermediates **14** derived from hexanal.[16] For example in the case of **15a**, the elimination is only about 50% complete after 60 h. In the cases of **15g**, **15l**, and **15n**, complete reaction required 12, 7, and 55 h, respectively. The decrease in the reaction rate was presumably due to the much weaker basicity of sodium hydroperoxide than that of NaOH.

The condensation reaction between allylborane **7** and hexanal was complete in less than 30 min. A slower reaction rate (9 h at room temperature) between **7** and cyclohexanone was observed (eq 4). Although cyclohexanone was found to react with **9** at the reflux temperature of THF (24 h) to form diene **28** after basic workup (58% yield), 2-pentanone failed to show any significant reactivity even after prolonged heating. However, by simply adding 5 drops of $BF_3{\cdot}OEt_2$ (ca. 0.2 mL for a 3-mmol reaction) to the reaction mixtures, condensation with cyclohexanone was essentially complete after only 2 h at room temperature and with 2-pentanone in 2 h at 35 °C (eqs 5 and 6).



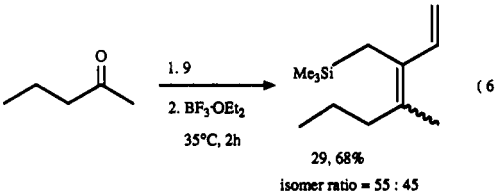
(4)

27, 67%



(5)

28, 61%



(6)

29, 68%

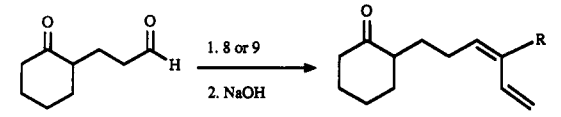
isomer ratio = 55 : 45

Presumably in the presence of $BF_3{\cdot}OEt_2$, the reaction takes a different pathway through an acyclic transition state with enhanced reaction rate.[3e] The Peterson olefination reaction was also simultaneously promoted by $BF_3{\cdot}OEt_2$[14,17] and the corresponding diene was produced without treating

(13) Brown, H. C.; Bhat, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 293–294.
(14) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464–1468.
(15) Kise, H.; Sato, T.; Yasuoka, T.; Seno, M.; Asahara, T. *J. Org. Chem.* **1979**, *44*, 4454–4456.
(16) The longer reaction time and higher reaction temperature required to promote the Peterson olefination reaction for the synthesis of internal 1,3-butadienes[3b] was also due to the presence of an excess H_2O_2. Indeed when only NaOH was used, the elimination of trimethylsilyl oxide to afford (2*Z*,4*Z*)-4-methyl-2,4-decadiene and (1*Z*,3*Z*)-2-methyl-1-phenyl-1,3-pentadiene was essentially complete in less than 4 and 1 h, respectively, at room temperature. The elimination reaction promoted by NaOEt required only 1 h and 30 min, respectively, at room temperature.
(17) Soderquist, J. A.; Santiago, B. *Tetrahedron Lett.* **1989**, *30*, 5693–5696.

with NaOH or H_2SO_4. Diene **29** derived from 2-pentanone was a 55:45 mixture of geometrical isomers. Apparently in this case the condensation step is not highly diastereoselective.

The lower reactivity of allylboranes toward the keto group was exploited for selective condensation with the aldehyde group of **30**[18] to form **31** (eq 7). The ester carbonyl was also much less reactive, and selective condensation was achieved with **32**,[19] (eq 8). Hydrolysis of **33a** produced the corresponding (*E*)-7-methyl-6,8-nonadienoic acid (**34**, *E*:*Z* = 96:4).

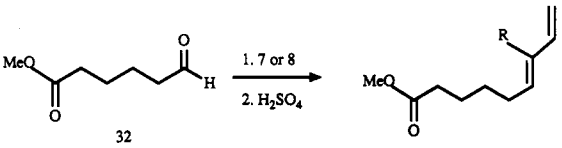


(7)

30

31a, R = *n*-Bu, 73% (*E* : *Z* = 4 : 96)

31b, R = Me_3SiCH_2, 87% (*E* : *Z* = 95 : 5)



(8)

32

33a, R = Me, 81% (*E* : *Z* = 96 : 4)

33b, R = *n*-Bu, 59% (*E* : *Z* = 96 : 4)

In conclusion, this procedure offers a simple and stereoselective route to a variety of terminal 1,3-butadienes. Substituents on these 1,3-butadienes can be easily varied by using different combinations of carbonyl compounds and allylboranes. The ability to obtain both isomers through the same condensation intermediate provides a unique versatility to the construction of further functionalized 1,3-butadienes for subsequent chemical transformations. Dienes derived from allylboranes **7** and **9** contain an isoprenyl unit, and therefore could find useful applications for the synthesis of natural products. It is also worth noting that 2-[(trimethylsilyl)methyl]-1,3-butadiene, the parent diene of those derived from **9**, exhibited extremely high regioselectivity in the Lewis acid catalyzed Diels–Alder reactions.[20] It has also been utilized to introduce an isoprenyl group to an electrophilic carbon atom.[21] The reaction sequence outlined in Scheme I has also been successfully adopted for the stereoselective synthesis of 2-(phenylthio)-1,3-butadienes.[3c]

Experimental Section

General procedures described in Chapter 9 of ref 22 for the manipulation of organoborane and other organometallic reagents were employed. All glassware, syringes, and needles were oven-dried at 140 °C for several hours. The glassware was assembled while hot and cooled under a stream of dry N_2. ^1H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded in $CDCl_3$, with Me_4Si, $CHCl_3$ (^1H δ 7.26), or $CDCl_3$ (^{13}C δ 77.02) as internal standard. The isomer ratios were determined by the integration of the ^1H NMR spectra. The nuclear Overhauser effect was measured by using the ^1H-homo gated decoupling method. Mass spectra were obtained at 70 eV. The melting point of (*Z*)-4,4-dimethyl-3-(trimethylsilyl)-2-penten-1-ol is uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, TN.

Materials. Tetrahydrofuran and diethyl ether were distilled from $LiAlH_4$ and stored under N_2. 9-Borabicyclo[3.3.1]nonane (9-BBN) was prepared according to the reported procedure.[23] Allenylsilanes were synthesized by the method reported previously.[4] Preparation of 1,2-bis(trimethylsilyl)-2,3-butadiene (**3**)[24] was carried out as previously described.[4d] Occasionally, the isolated allenylsilanes were found to be slightly contaminated with the corresponding trimethylsilyl-substituted acetylenes and other minor impurities. Except in the case of **4**, we found that these impurities could be easily removed by treatment with NaOEt in ethanol at room temperature for 3 h. Allene **4** was also susceptible to attack by NaOEt and was completely destroyed under the reaction condition. Allylboranes **7–12** were prepared in situ for the NMR studies by adding 0.5 mmol of the corresponding allenylsilanes dissolved in 0.4 mL of THF-d_8 or toluene-d_8 to 0.5 mmol of solid 9-BBN (0.061 g) at room temperature. The hydroboration reaction was essentially complete within 2 h in the cases of **1–4**. The ^1H NMR spectra of **11** and **12** were taken after 18 and 50 h, respectively. The ^1H NMR chemical shifts are reported using internal THF-d_7 (δ 3.58) or internal toluene-d_7 (δ 2.09) as reference. The ^{11}B NMR chemical shifts are relative to external BF_3·OEt_2. Hexanal, benzaldehyde, acetaldehyde, and ketones were obtained from the Aldrich Chemical Co., Inc., and were distilled prior to use. Keto aldehyde **30**[18] and methyl 6-oxohexanoate (**32**)[19] were prepared as described previously. *n*-Butyllithium in hexane and *tert*-butyllithium in pentane were also purchased from Aldrich and were used after the concentrations were standardized. Crotonaldehyde, chlorotrimethylsilane, (chloromethyl)trimethylsilane, THF-d_8, methylmagnesium chloride in THF (3.0 M), isopropylmagnesium chloride in THF (2.0 M), *tert*-butylmagnesium chloride in THF (2.0 M), Red-Al in toluene (3.4 M), and propargyl alcohol were also obtained from Aldrich and were used directly without further purification. Toluene-d_8 was purchased from Aldrich and was distilled from CaH_2 prior to use.

1,3-Butadienes. (*Z*)-3-Methyl-1,3-nonadiene (15a). The following procedure for the synthesis of **15a** is representative for those dienes obtained by basic workup. To 0.47 g of 3-(trimethylsilyl)-1,2-butadiene (**1**) (3.7 mmol) in 10 mL of THF was introduced by a syringe 6.5 mL of a 0.57 M solution of 9-BBN (3.7 mmol) in THF at room temperature. After 2 h of stirring,[25] 0.44 mL of hexanal (0.37 g, 3.7 mmol) was introduced. After an additional 30 min of stirring,[26] the reaction mixture was treated with 5.0 mL of 3 N NaOH.[27] The elimination of trimethylsilyl oxide was complete after 2 h.[28] Hydrogen peroxide (30%, 1 mL) was then introduced to oxidize the organoborane byproduct. Hexane (20 mL) was added, and the organic layer was then separated, washed with water, and concentrated. The residue was passed through a short column (silica gel/hexane) and was distilled on a short-path distilling head to afford 0.37 g (73%) of **15a** (*Z*:*E* = 95:5) as a colorless liquid: IR (neat) 1635 (w), 1590 (m), 1450 (s), 1430 (m), 1370 (m), 1115 (m), 1075 (m), 980 (s), 900 (s), 850 (m), 720 (w), 690 (w) cm^{-1}; ^1H NMR δ 6.78 (1 H, ddd, *J* = 17.4, 10.8, and 1 Hz), 5.39 (1 H, t, *J* = 7.5 Hz), 5.17 (1 H, d,

(18) (a) Cope, A. C.; Nealy, D. L.; Scheiner, P.; Wood, G. *J. Am. Chem. Soc.* **1965**, *87*, 3130–3135. (b) Allan, R. D.; Cordiner, B. G.; Wells, R. J. *Tetrahedron Lett.* **1968**, 6055–6056.

(19) Bosone, E.; Farina, P.; Guazzi, G. *Synthesis* **1983**, 942–944.

(20) Hosomi, A.; Iguchi, H.; Sasaki, J.; Sakurai, H. *Tetrahedron Lett.* **1982**, *23*, 551–554.

(21) Hosomi, A.; Saito, M.; Sakurai, H. *Tetrahedron Lett.* **1979**, 429–432.

(22) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.

(23) Soderquist, J.; Brown, H. C. *J. Org. Chem.* **1981**, *46*, 4599–4600.

(24) 1,2-Bis(trimethylsilyl)-2,3-butadiene (**3**) was synthesized in 60% yield from chloromethyltrimethylsilane: bp 42 °C (2.5 Torr); IR (neat) 1925 (s), 1630 (w), 1410 (m), 1250 (s), 1150 (w), 990 (m), 845 (s), 750 (m), 690 (m) cm^{-1}; ^1H NMR δ 4.28 (2 H, t, *J* = 2.8 Hz), 1.25 (2 H, t, *J* = 2.8 Hz), 0.08 (9 H, s), 0.05 (9 H, s); ^{13}C NMR δ 208.74, 90.60, 68.45, 16.08, −0.81, −1.66; MS *m*/*e* 198 (M^+, 18), 183 (15), 155 (6), 110 (50), 95 (10), 83 (6), 73 (100).

(25) The hydroboration reaction was complete within 2 h with allenes **1–4**. In the case of **5**, the reaction mixture was stirred at room temperature for 18 h. With allene **6**, the reaction mixture was heated at reflux for 24 h.

(26) For all other cases with allylboranes **7–10**, the reaction mixture was stirred at room temperature for 1 h. The condensation reaction with allylboranes **11** and **12** was carried out at room temperature for 2 and 24 h, respectively.

(27) In the cases where NaOEt was used to promote the Peterson olefination reaction, the reaction mixture was transferred via cannula to a separate flask containing 11 mmol of NaOEt and 10 mL of THF.

(28) See Table I for the length of time in other cases.

J = 17.4 Hz), 5.06 (1 H, dt, J = 10.8 and 1.6 Hz), 2.15 (2 H, q, J = 7.0 Hz), 1.81 (3 H, d, J = 1.3 Hz), 1.4–1.25 (6 H, br), 0.89 (3 H, t); ^{13}C NMR δ 133.86, 132.13, 131.61, 113.09, 31.60, 29.65, 27.38, 22.65, 19.79, 14.09. Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 87.13; H, 13.17.

(*E*)-3-Methyl-1,3-nonadiene (16a).[29] The same procedure was repeated as for **15a**, except that 5 drops of concentrated sulfuric acid was introduced to induce the Peterson olefination reaction. The reaction mixture was stirred at room temperature for 1 h[28] before workup with alkaline H_2O_2. Purification by column chromatography and distillation afforded **16a** as a colorless liquid: IR (neat) 1630 (m), 1600 (m), 1450 (s), 1370 (m), 1250 (m), 1075 (s), 1010 (m), 980 (s), 885 (s), 860 (m), 800 (m), 720 (w) cm^{-1}; ^{1}H NMR δ 6.38 (1 H, dd, J = 17.4 and 10.6 Hz), 5.50 (1 H, t, J = 7.3 Hz), 5.08 (1 H, d, J = 17.4 Hz), 4.92 (1 H, d, J = 10.8 Hz), 2.13 (2 H, q, J = 7 Hz), 1.74 (3 H, s), 1.45–1.25 (6 H, br), 0.90 (3 H, t); ^{13}C NMR δ 141.71, 133.84, 133.56, 110.22, 31.62, 29.23, 28.23, 22.61, 14.07, 11.63.

(*Z*)-2-Methyl-1-phenyl-1,3-butadiene (15b):[30] IR (neat) 1940 (w), 1875 (w), 1805 (m), 1595 (s), 1485 (m), 1435 (s), 1370 (m), 1220 (m), 1070 (m), 1050 (m), 1020 (m), 1000 (s), 905 (s), 855 (m), 840 (m), 785 (m), 745 (s), 700 (s) cm^{-1}; ^{1}H NMR δ 7.35–7.20 (5 H, m), 6.89 (1 H, dd, J = 17.3 and 10.9 Hz), 6.49 (1 H, s), 5.35 (1 H, dm, J = 17.4 and 1 Hz), 5.16 (1 H, dm, J = 10.8 and 1 Hz), 2.00 (3 H, d, J = 1 Hz); ^{13}C NMR δ 137.56, 135.07, 134.87, 129.88, 129.37, 128.05, 126.55, 115.37, 20.40; MS m/e 144 (M$^+$, 41), 129 (100), 128 (48), 127 (16), 115 (22), 105 (7), 91 (14), 77 (12).

(*E*)-2-Methyl-1-phenyl-1,3-butadiene (16b):[3f] IR (neat) 1940 (w), 1880 (w), 1790 (w), 1595 (m), 1480 (m), 1435 (m), 1380 (w), 1350 (w), 1290 (w), 1070 (m), 1050 (m), 1020 (m), 980 (s), 890 (s), 860 (m), 740 (s), 690 (s) cm^{-1}; ^{1}H NMR δ 7.38–7.18 (5 H, m), 6.55 (1 H, dd, J = 17.4 and 10.6 Hz), 6.53 (1 H, s), 5.30 (1 H, d, J = 17.2 Hz), 5.13 (1 H, d, J = 10.6 Hz), 2.00 (3 H, s); ^{13}C NMR δ 141.89, 137.74, 135.97, 131.63, 129.20, 128.10, 126.60, 112.92, 13.16; MS m/e 144 (M$^+$, 76), 129 (100), 128 (36), 127 (13), 115 (23), 105 (10), 91 (20), 77 (12).

(*Z*)-3-Butyl-1,3-nonadiene (15c): IR (neat) 1630 (w), 1590 (m), 1450 (s), 1370 (m), 1250 (w), 1120 (w), 1100 (w), 985 (s), 900 (s), 855 (m), 840 (m), 730 (m) cm^{-1}; ^{1}H NMR δ 6.68 (1 H, dd, J = 17.6 and 11.0 Hz), 5.38 (1 H, t, J = 7.2 Hz), 5.21 (1 H, d, J = 17.6 Hz), 5.07 (1 H, d, J = 11.0 Hz), 2.2–2.1 (4 H, m), 1.5–1.2 (10 H, m), 0.92 (3 H, t), 0.90 (3 H, t); ^{13}C NMR δ 136.48, 133.02, 130.73, 112.73, 33.08, 31.56, 31.15, 29.67, 27.38, 22.72, 22.60, 14.08, 14.02.

(*E*)-3-Butyl-1,3-nonadiene (16c): IR (neat) 1630 (m), 1600 (m), 1455 (s), 1375 (m), 1245 (w), 1100 (m), 985 (s), 890 (s), 860 (m), 835 (m), 725 (w) cm^{-1}; ^{1}H NMR δ 6.26 (1 H, dd, J = 17.6 and 10.8 Hz), 5.45 (1 H, t, J = 7.3 Hz), 5.09 (1 H, d, J = 17.6 Hz), 4.91 (1 H, d, J = 10.6 Hz), 2.22 (2 H, t, J = 7.5 Hz), 2.11 (2 H, q, J = 7 Hz), 1.4–1.2 (10 H, m), 0.90 (6 H, m); ^{13}C NMR δ 140.59, 138.63, 133.47, 110.07, 31.68, 31.25, 29.39, 28.16, 26.00, 23.07, 22.62, 14.04 (2 carbons).

(*Z*)-2-Butyl-1-phenyl-1,3-butadiene (15d): IR (neat) 1940 (w), 1880 (w), 1810 (w), 1595 (m), 1490 (m), 1455 (m), 1440 (m), 1410 (w), 1370 (w), 1100 (w), 1070 (w), 1030 (w), 1000 (m), 900 (s), 845 (w), 780 (w), 745 (s), 700 (s) cm^{-1}; ^{1}H NMR δ 7.35–7.15 (5 H, m), 6.79 (1 H, dd, J = 17.6 and 11.2 Hz), 6.46 (1 H, s), 5.37 (1 H, d, J = 17.6 Hz), 5.15 (1 H, dm, J = 11.0 and 1 Hz), 2.36 (2 H, t, J = 7.5 Hz), 1.55 (2 H, quintet, J = 7 Hz), 1.39 (2 H, sextet, J = 7 Hz), 0.94 (3 H, t, J = 7.1 Hz); ^{13}C NMR δ 139.20, 137.70, 134.27, 129.41, 129.07, 127.99, 126.47, 114.87, 33.59, 31.15, 22.75, 14.04.

(*E*)-2-Butyl-1-phenyl-1,3-butadiene (16d): IR (neat) 1940 (w), 1880 (w), 1800 (w), 1600 (s), 1490 (m), 1460 (s), 1410 (w), 1375 (m), 1300 (w), 1180 (w), 1100 (m), 1070 (m), 1030 (m), 985 (s), 900 (s), 870 (m), 750 (s), 695 (s) cm^{-1}; ^{1}H NMR δ 7.4–7.15 (5 H, m), 6.47 (1 H, s), 6.43 (1 H, ddd, J = 17.4, 10.6, and 1 Hz), 5.31 (1 H, dd, J = 17.4 and 1 Hz), 5.12 (1 H, dd, J = 10.7 and 1 Hz), 2.44 (2 H, t, J = 8 Hz), 1.6–1.47 (2 H, m), 1.39 (2 H, sextet, J = 7.3 Hz), 0.93 (3 H, t, J = 7.1 Hz); ^{13}C NMR δ 141.01, 140.89, 137.73, 131.19, 128.77, 128.22, 126.63, 112.76, 31.32, 26.68, 23.10, 13.89.

(3*Z*,5*E*)-3-Butyl-1,3,5-heptatriene (15e): IR (neat) 1605 (w), 1570 (w), 1450 (m), 1370 (m), 980 (s), 960 (s), 930 (m), 895 (s) cm^{-1}; ^{1}H NMR δ 6.85 (1 H, dd, J = 17.4 and 11.0 Hz), 6.52 (1 H, ddq, J = 14.9, 11.3, and 1.7 Hz), 5.95 (1 H, d, J = 11.4 Hz), 5.70 (1 H, dq, J = 14.7 and 6.8 Hz), 5.24 (1 H, d, J = 17.4 Hz), 5.10 (1 H, d, J = 11.0 Hz), 2.22 (2 H, t, J = 7.5 Hz), 1.80 (3 H, d, J = 7 Hz), 1.5–1.4 (2 H, m), 1.33 (2 H, sextet, J = 7 Hz), 0.91 (3 H, t, J = 7 Hz); ^{13}C NMR δ 135.99, 132.67, 129.57, 129.03, 127.04, 113.29, 33.00, 31.18, 22.76, 18.46, 14.01.

(*E*)-3-[(Trimethylsilyl)methyl]-1,3-pentadiene (15f):[31] IR (neat) 1640 (w), 1600 (w), 1430 (w), 1250 (s), 1160 (m), 985 (m), 960 (w), 890 (m), 835 (s), 685 (m) cm^{-1}; ^{1}H NMR δ 6.75 (1 H, ddd, J = 17.4, 11.0, and 1 Hz), 5.27 (1 H, qm, J = 7.1 and 1 Hz), 5.12 (1 H, d, J = 17 Hz), 5.07 (1 H, d, J = 11 Hz), 1.74 (3 H, d, J = 7.1 Hz), 1.63 (2 H, quintet, J = 1 Hz), –0.02 (9 H, s); ^{13}C NMR δ 134.75, 133.45, 122.67, 113.29, 22.38, 13.06, –1.01; MS m/e 154 (M$^+$, 21), 139 (8), 111 (5), 97 (5), 85 (4), 79 (3), 74 (24), 73 (100).

(*Z*)-3-[(Trimethylsilyl)methyl]-1,3-pentadiene (16f):[31] IR (neat) 1630 (w), 1605 (w), 1420 (w), 1350 (w), 1260 (m), 1245 (s), 1165 (m), 985 (m), 885 (m), 845 (s), 690 (w), 650 (w) cm^{-1}; ^{1}H NMR δ 6.32 (1 H, dd, J = 17.4 and 10.7 Hz), 5.47 (1 H, q, J = 7.0 Hz), 4.98 (1 H, d, J = 17.4 Hz), 4.89 (1 H, d, J = 10.8 Hz), 1.72 (2 H, s), 1.67 (3 H, d, J = 7.0 Hz), 0.01 (9 H, s); ^{13}C NMR δ 141.61, 137.28, 124.48, 10.31, 16.06, 14.45, –0.46; MS m/e 154 (M$^+$, 22) 139 (8), 111 (5), 97 (5), 85 (4), 79 (3), 74 (26), 73 (100).

(*E*)-3-[(Trimethylsilyl)methyl]-1,3-nonadiene (15g): IR (neat) 1630 (w), 1590 (m), 1460 (m), 1240 (s), 1155 (s), 1005 (m), 980 (s), 890 (s), 840 (s), 760 (m), 720 (m), 685 (s) cm^{-1}; ^{1}H NMR δ 6.74 (1 H, ddd, J = 17.4, 11.0, and 0.8 Hz), 5.21 (1 H, tm, J = 7.5 and 1 Hz), 5.11 (1 H, dm, J = 17 and 1 Hz), 5.06 (1 H, dm, J = 11 and 1 Hz), 2.16 (2 H, q, J = 7 Hz), 1.63 (2 H, d, J = 1 Hz), 1.30 (6 H, br), 0.89 (3 H, t), –0.02 (9 H, s); ^{13}C NMR δ 133.81, 133.76, 129.38, 113.35, 31.55, 29.96, 27.42, 22.60, 22.33, 14.11, –0.99; MS m/e 210 (M$^+$, 3), 195 (1), 153 (2), 136 (1), 125 (2), 73 (100).

(*Z*)-3-[(Trimethylsilyl)methyl]-1,3-nonadiene (16g): IR (neat) 1630 (w), 1595 (m), 1460 (m), 1375 (m), 1245 (s), 1160 (m), 1010 (m), 985 (m), 895 (s), 840 (s), 690 (m) cm^{-1}; ^{1}H NMR δ 6.31 (1 H, dd, J = 17.4 and 11.0 Hz), 5.36 (1 H, t, J = 7 Hz), 4.98 (1 H, d, J = 17.4 Hz), 4.91 (1 H, d, J = 10.8 Hz), 2.05 (2 H, q, J = 7 Hz), 1.71 (2 H, s), 1.31 (6 H, br), 0.90 (3 H, t), 0.01 (9 H, s); ^{13}C NMR δ 141.80, 135.92, 131.06, 110.46, 31.77, 29.32, 28.86, 22.66, 16.40, 14.08, –0.46; MS m/e 210 (M$^+$, 4), 195 (1), 153 (2), 136 (1), 125 (3), 73 (100).

(*E*)-2-[(Trimethylsilyl)methyl]-1-phenyl-1,3-butadiene (15h): IR (neat) 1620 (w), 1600 (s), 1585 (m), 1490 (s), 1445 (m), 1420 (m), 1245 (s), 1225 (m), 1200 (m), 1155 (s), 1000 (m), 900 (s), 850 (s), 740 (s), 695 (s) cm^{-1}; ^{1}H NMR δ 7.34–7.15 (5 H, m), 6.86 (1 H, ddd, J = 17.4, 10.9, and 0.9 Hz), 6.31 (1 H, br s), 5.29 (1 H, dm, J = 17.4 and 1 Hz), 5.16 (1 H, dt, J = 11.0 and 1.5 Hz), 1.85 (2 H, d, J = 1 Hz), 0.06 (9 H, s); ^{13}C NMR δ 138.04, 137.25, 135.17, 129.40, 128.05, 127.74, 126.21, 115.67, 23.54, –0.89; MS m/e 216 (M$^+$, 11), 201 (3), 142 (14), 129 (12), 115 (3), 73 (100). Anal. Calcd for $C_{14}H_{20}Si$: C, 77.70; H, 9.32. Found: C, 77.16; H, 9.61.

(*Z*)-2-[(Trimethylsilyl)methyl]-1-phenyl-1,3-butadiene (16h): IR (neat) 1605 (m), 1495 (m), 1445 (m), 1250 (s), 1150 (m), 985 (m), 895 (m), 845 (s), 745 (m), 695 (s) cm^{-1}; ^{1}H NMR δ 7.31 (4 H, d, J = 4.4 Hz), 7.17 (1 H, m), 6.47 (1 H, ddd, J = 17.4, 10.8, and 0.7 Hz), 6.39 (1 H, br s), 5.21 (1 H, d, J = 17.2 Hz), 5.10 (1 H, d, J = 10.8 Hz), 2.09 (2 H, s), –0.04 (9 H, s); ^{13}C NMR δ 142.37, 138.85, 135.48, 128.95, 128.90, 128.19, 126.30, 113.03, 16.91, –0.39; MS m/e 216 (M$^+$, 11), 201 (3), 142 (15), 129 (13), 115 (3), 73 (100).

(3*E*,5*E*)-3-[(Trimethylsilyl)methyl]-1,3,5-heptatriene (15i): IR (neat) 1610 (w), 1570 (w), 1415 (m), 1375 (w), 1350 (w), 1285 (m), 1245 (s), 1210 (m), 1160 (m), 1010 (m), 980 (s), 955 (s), 925 (m), 890 (s), 880 (s), 845 (s), 760 (w), 695 (m) cm^{-1}; ^{1}H NMR δ 6.90 (1 H, dd, J = 17.2 and 10.8 Hz), 6.52 (1 H, ddq, J = 14.8, 11.3, and 1.7 Hz), 5.79 (1 H, dt, J = 11.2 and 1 Hz), 5.60 (1 H, dq, J = 14.5 and 6.9 Hz), 5.13 (1 H, d, J = 17 Hz), 5.09 (1 H, dt, J = 11 and 1.5 Hz), 1.79 (3 H, dd, J = 6.8 and 1.3 Hz), 1.68 (2 H, s), –0.01 (9 H, s); ^{13}C NMR δ 133.76, 133.37, 128.08, 127.70, 127.16, 113.84, 22.85, 18.41, –0.97; MS m/e 180 (M$^+$, 14), 165 (2), 149 (1), 123 (1), 106 (12), 91 (4), 83 (1), 73 (100), 59 (13).

(*E*)-3-Phenyl-1,3-nonadiene (15j): IR (neat) 1630 (w), 1590 (m), 1490 (s), 1460 (s), 1440 (s), 1410 (w), 1370 (w), 1340 (w), 1070 (m), 1030 (m), 985 (s), 910 (s), 860 (w), 840 (w), 770 (s), 700 (s)

(29) Garbers, C. F.; Scott, F. *Tetrahedron Lett.* **1976**, 507–510.
(30) Mauze, B.; Ongoka, P.; Miginiac, L. *J. Organomet. Chem.* **1984**, *264*, 1–7.
(31) Djahanbini, D.; Cazes, B.; Gore, J. *Tetrahedron* **1985**, *41*, 867–873.

cm^{-1}; ^1H NMR δ 7.35–7.25 (5 H, m), 6.85 (1 H, ddd, J = 17.4, 10.8, and 1.7 Hz), 5.56 (1 H, t, J = 7.6 Hz), 5.21 (1 H, dt, J = 10.8 and 1.7 Hz), 5.06 (1 H, dd, J = 17.4 and 1.5 Hz), 2.30 (2 H, q, J = 7 Hz), 1.5–1.4 (2 H, m), 1.38–1.25 (4 H, m), 0.90 (3 H, t); ^{13}C NMR δ 141.77, 139.75, 133.28, 132.21, 128.87, 127.95, 126.75, 117.08, 31.57, 29.42, 28.09, 22.60, 14.08; MS m/e 200 (M^+, 46), 157 (18), 143 (100), 130 (74), 129 (60), 128 (71), 116 (21), 115 (57), 105 (11), 91 (29), 77 (12). Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.41; H, 9.57.

(*Z*)-3-Phenyl-1,3-nonadiene (16j): IR (neat) 1630 (m), 1605 (s), 1500 (s), 1460 (s), 1440 (s), 1410 (m), 1380 (m), 1080 (s), 1030 (m), 990 (s), 910 (s), 770 (s), 705 (s) cm^{-1}; ^1H NMR δ 7.38–7.22 (3 H, m), 7.11 (2 H, dt, J = 6.6 and 1.5 Hz), 6.55 (1 H, dd, J = 17.3 and 10.5 Hz), 5.71 (1 H, t, J = 7.5 Hz), 4.96 (1 H, dm, J = 10.4 and 0.6 Hz), 4.66 (1 H, dm, J = 17.4 and 0.6 Hz), 1.92 (2 H, q, J = 7.3 Hz), 1.33 (2 H, quintet), 1.25–1.15 (4 H, m), 0.83 (3 H, t); ^{13}C NMR δ 141.50, 140.86, 137.93, 134.22, 129.57, 128.05, 126.72, 114.08, 31.44, 29.36, 29.02, 22.51, 13.98; MS m/e 200 (M^+, 45), 157 (31), 143 (100), 130 (73), 129 (65), 128 (76), 116 (30), 115 (74), 105 (24), 91 (40), 77 (21).

(*E*)-1,2-Diphenyl-1,3-butadiene (15k):[32] IR (neat) 1590 (m), 1490 (m), 1440 (m), 1070 (m), 1020 (m), 1000 (m), 910 (s), 760 (s), 740 (s), 710 (s) cm^{-1}; ^1H NMR δ 7.4–7.15 (10 H, m), 7.02 (1 H, ddd, J = 17.5, 10.9, and 1 Hz), 6.56 (1 H, s), 5.30 (1 H, dt, J = 10.8 and 1.7 Hz), 5.22 (1 H, dd, J = 17.4 and 1.5 Hz); ^{13}C NMR δ 141.72, 141.31, 137.27, 134.67, 130.85, 129.54, 129.15, 128.11, 128.06, 127.34, 127.01, 119.64; MS m/e 206 (m^+, 100), 191 (24), 178 (12), 165 (11), 128 (27), 91 (64), 77 (16).

(*Z*)-1,2-Diphenyl-1,3-butadiene (16k):[32] IR (KBr) 1600 (m), 1495 (m), 1450 (m), 1080 (m), 1030 (m), 990 (m), 910 (m), 890 (w), 785 (m), 760 (m), 700 (s) cm^{-1}; ^1H NMR δ 7.5–6.85 (10 H, m), 6.74 (1 H, dd, J = 17.2 and 10.4 Hz), 6.60 (1 H, s), 5.15 (1 H, d, J = 10.3 Hz), 4.84 (1 H, d, J = 17.2 Hz); ^{13}C NMR δ 141.81, 141.77, 137.94, 136.71, 131.49, 129.63, 129.43, 128.76, 127.95, 127.29, 126.90, 116.40.

(*E*)-3-(1-Methylethyl)-1,3-nonadiene (15l): IR (neat) 1625 (w), 1590 (w), 1450 (s), 1370 (m), 1350 (m), 1100 (w), 980 (s), 890 (s), 850 (w), 720 (w) cm^{-1}; ^1H NMR δ 6.63 (1 H, dd, J = 17.6 and 11.2 Hz), 5.37 (1 H, t, J = 7.3 Hz), 5.21 (1 H, dd, J = 17.6 and 1 Hz), 5.07 (1 H, dt, J = 11.2 and 1.5 Hz), 2.63 (1 H, septet, J = 6.8 Hz), 2.15 (2 H, q, J = 7 Hz), 1.30 (6 H, br), 1.05 (6 H, d, J = 6.8 Hz), 0.89 (3 H, t); ^{13}C NMR δ 142.54, 133.19, 127.11, 112.61, 31.60, 29.78, 29.05, 27.46, 22.63, 22.49, 14.10; MS m/e 166 (M^+, 31), 151 (3), 137 (14), 123 (41), 109 (47), 96 (26), 95 (35), 81 (100). Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.43; H, 13.24.

(*Z*)-3-(1-Methylethyl)-1,3-nonadiene (16l): IR (neat) 1625 (m) 1605 (m), 1460 (s), 1410 (m), 1380 (s), 1360 (s), 1310 (w), 1245 (w), 1160 (w), 1100 (m), 990 (s), 905 (s), 860 (m), 840 (m), 730 (w), cm^{-1}; ^1H NMR δ 6.24 (1 H, ddd, J = 17.4, 11.0 and 1 Hz), 5.46 (1 H, t, J = 7.5 Hz), 5.25 (1 H, dd, J = 17.4 and 2.0 Hz), 4.91 (1 H, dd, J = 11.0 and 1.8 Hz), 2.86 (1 H, septet, J = 7.0 Hz), 2.09 (2 H, q, J = 7.3 Hz), 1.31 (6 H, br), 1.06 (6 H, d, J = 7.1 Hz), 0.89 (3 H, t); ^{13}C NMR δ 143.93, 137.67, 127.82, 112.20, 31.67, 29.65, 27.72, 27.59, 22.62, 21.29, 14.50; MS m/e 166 (M^+, 34), 151 (5), 137 (20), 123 (56), 109 (56), 96 (28), 95 (45), 81 (100).

(*E*)-2-(1-Methylethyl)-1-phenyl-1,3-butadiene (15m): IR (neat) 1620 (w), 1600 (m), 1490 (m), 1460 (s), 1410 (w), 1380 (m), 1360 (m), 1150 (m), 1105 (m), 1080 (m), 1030 (m), 1000 (s), 905 (s), 850 (m), 780 (m), 750 (m), 720 (s), 700 (s) cm^{-1}; ^1H NMR δ 7.35–7.2 (5 H, m), 6.76 (1 H, dd, J = 17.8 and 11.4 Hz), 6.46 (1 H, s), 5.38 (1 H, d, J = 17.6 Hz), 5.15 (1 H, dm, J = 11.2 and 1 Hz), 2.83 (1 H, septet, J = 6.8 Hz), 1.19 (6 H, d, J = 6.8 Hz); ^{13}C NMR δ 145.22, 137.97, 134.54, 129.49, 127.95, 126.40, 125.98, 114.24, 29.58, 22.53; MS m/e 172 (M^+, 7), 157 (5), 143 (3), 142 (7) 129 (100), 115 (9), 91 (7), 77 (6).

(*Z*)-2-(1-Methylethyl)-1-phenyl-1,3-butadiene (16m): IR (neat) 1600 (m), 1490 (m), 1460 (m), 1440 (m), 1410 (m), 1380 (m), 1360 (m), 1150 (w), 1100 (m), 1070 (m), 1020 (m), 1000 (s), 980 (s), 910 (s), 870 (m), 760 (s), 700 (s) cm^{-1}; ^1H NMR δ 7.35–7.20 (5 H, m), 6.58 (1 H, s), 6.42 (1 H, ddd, J = 17.2, 11.0, and 1 Hz), 5.51 (1 H, dd, J = 17.3 and 1.7 Hz), 5.11 (1 H, dd, J = 11.0 and 1.8 Hz), 3.14 (1 H, septet, J = 7.0 Hz), 1.11 (6 H, d, J = 7.0 Hz); ^{13}C NMR δ 146.61, 138.02, 136.63, 128.88, 128.12, 126.40, 125.33, 114.78, 28.04, 21.50.

(*E*)-3-(1,1-Dimethylethyl)-1,3-nonadiene (15n): NaOH workup; IR (neat, *E*:*Z* = 41:59) 1610 (w), 1460 (s), 1410 (w), 1390 (w), 1380 (w), 1360 (s), 1250 (w), 1200 (w), 990 (m), 920 (m), 910 (s), 870 (w), 840 (w) cm^{-1}; ^1H NMR (*E* isomer, minor) δ 6.20 (1 H, ddm, J = 17.6, 11.4, and 1 Hz), 5.32 (1 H, t, J = 7.1 Hz), 5.24 (1 H, dd, J = 11.3 and 2.6 Hz), 5.00 (1 H, dd, J = 17.6 and 2.6 Hz), 2.11 (2 H, q, J = 7 Hz), 1.3 (6 H, br m), 1.04 (9 H, s), 0.88 (3 H, t); ^{13}C NMR (*E* isomer, minor) δ 147.27, 134.66, 123.70, 117.88, 35.26, 31.65, 30.26, 29.64, 29.19, 22.64, 14.09. Anal. Calcd for $C_{13}H_{24}$: C, 86.59; H, 13.41. Found: C, 85.98; H, 13.74.

(*Z*)-3-(1,1-Dimethylethyl)-1,3-nonadiene (16n): H_2SO_4 workup; IR (neat, *E*:*Z* = 72:28) 1620 (w), 1460 (s), 1410 (w), 1390 (w), 1380 (w), 1360 (s), 1250 (w), 1200 (w), 990 (m), 920 (s), 910 (m), 870 (w), 840 (w) cm^{-1}; ^1H NMR (*Z* isomer, minor) δ 6.42 (1 H, ddq, J = 16.7, 10.4, and 1.1 Hz), 5.40 (1 H, td, J = 7.4 and 1.1 Hz), 5.08 (1 H, ddd, J = 16.7, 2.6, and 0.4 Hz), 4.80 (1 H, dd, J = 10.4 and 2.5 Hz), 2.22 (2 H, q, J = 7 Hz), 1.3 (6 H, br m), 1.15 (9 H, s), 0.90 (3 H, t); ^{13}C NMR (*Z* isomer, minor) δ 146.94, 141.41, 127.98, 112.51, 34.93, 31.73, 30.68, 30.30, 29.70, 22.68, 14.09.

(*E*)-2-(1,1-Dimethylethyl)-1-phenyl-1,3-butadiene (15o): NaOH workup; IR (neat, *E*:*Z* = 41:59) 1620 (w), 1595 (m), 1490 (m), 1475 (s), 1460 (m), 1440 (m), 1410 (w), 1390 (w), 1360 (s), 1245 (w), 1200 (m), 1070 (w), 1040 (w), 1030 (w), 1010 (w), 990 (m), 915 (s), 860 (m), 760 (s), 740 (w), 700 (s) cm^{-1}; ^1H NMR (*E* isomer, minor) δ 7.35–7.15 (5 H, m), 6.39 (1 H, ddd, J = 17.9, 11.5, and 0.9 Hz), 6.38 (1 H, s), 5.15 (1 H, ddd, J = 11.5, 2.2, and 0.6 Hz), 5.05 (1 H, dd, J = 17.9 and 2.4 Hz), 1.18 (9 H, s); ^{13}C NMR (*E* isomer, minor) 149.70, 138.70, 134.74, 129.63, 127.75, 125.92, 123.60, 119.20, 36.19, 29.65. Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.05; H, 10.01. In addition to diene isomers, about 20% of the trimethylsilyl ether of 2-(1,1-dimethylethyl)-1-phenyl-2-buten-1-ol was also isolated.

(*Z*)-2-(1,1-Dimethylethyl)-1-phenyl-1,3-butadiene (16o): H_2SO_4 workup (*E*:*Z* = 62:38); ^1H NMR (*Z* isomer, minor) δ 7.3–7.1 (5 H, m), 6.67 (1 H, s), 6.57 (1 H, ddd, J = 16.7, 10.5, and 1.1 Hz), 5.34 (1 H, dd, J = 16.7 and 2.2 Hz), 5.00 (1 H, dd, J = 10.4 and 2.2 Hz), 1.00 (9 H, s); ^{13}C NMR (*Z* isomer, minor) 149.81, 140.67, 140.52, 128.84, 127.55, 126.02, 125.58, 114.30, 35.97, 31.17. In addition to diene isomers, about 10% of the trimethylsilyl ether of 2-(1,1-dimethylethyl)-1-phenyl-2-buten-1-ol was also isolated.

2-Methyl-1,1-pentamethylene-1,3-butadiene (27): IR (neat) 1630 (s), 1600 (w), 1445 (s), 1420 (w), 1380 (w), 1350 (w), 1280 (w), 1260 (w), 1230 (m), 1190 (w), 1120 (w), 1070 (m), 1020 (w), 1010 (w), 980 (s), 890 (s), 850 (m), 710 (w), 690 (w) cm^{-1}; ^1H NMR δ 6.94 (1 H, dd, J = 17.1 and 10.9 Hz), 5.14 (1 H, dd, J = 17.2 and 1.7 Hz), 5.00 (1 H, dd, J = 10.9 and 1.6 Hz), 2.36 (2 H, br t), 2.30 (2 H, br t), 1.80 (3 H, s), 1.58 (6 H, br s); ^{13}C NMR δ 140.16, 135.29, 123.42, 111.48, 31.72, 30.15, 28.26, 28.13, 26.98, 13.13.

1,1-Pentamethylene-2-[(trimethylsilyl)methyl]-1,3-butadiene (28): IR (neat) 1620 (w), 1445 (w), 1245 (s), 1160 (w), 995 (w), 980 (w), 890 (m), 835 (s), 685 (w) cm^{-1}; ^1H NMR δ 6.88 (1 H, dd, J = 17.2 and 11.0 Hz), 5.04 (1 H, dd, J = 17.2 and 1.5 Hz), 4.98 (1 H, dd, J = 11.0 and 1.5 Hz), 2.35 (2 H, t), 2.19 (2 H, t), 1.75 (2 H, s), 1.55 (6 H, br), –0.01 (9 H, s); ^{13}C NMR δ 137.13, 135.23, 125.91, 112.05, 32.27, 30.20, 28.42, 28.00, 27.04, 17.10, –0.41; MS m/e 208 (M^+, 12), 193 (3), 179 (2), 134 (8), 119 (6), 106 (3), 105 (4), 93 (5), 92 (7), 91 (7), 85 (2), 79 (3), 73 (100).

4-Methyl-3-[(trimethylsilyl)methyl]-1,3-heptadiene (29, isomer ratio = 55:45): IR (neat) 1620 (w), 1590 (w), 1450 (w), 1420 (w), 1370 (w), 1240 (s), 1160 (m), 980 (m), 885 (s), 835 (s), 685 (m) cm^{-1}; ^1H NMR δ 6.81 (H_2C=C*H*, dd, J = 17.2 and 11.0 Hz), 6.795 (H_2C=C*H*, dd, J = 17.4 and 10.8 Hz), 5.04–4.94 (H_2C=CH, m), 2.18 (C=C(CH$_3$)CH_2, t), 2.04 (C=C(CH$_3$)CH_2, t), 1.80 (CH$_3$C=C, s), 1.73 (CH$_3$C=C and Me$_3$SiCH_2, m), 1.42 (CH$_3$CH_2, sextet), 0.92 (CH_3CH$_2$, t), 0.90 (CH_3CH$_2$, t), –0.01 (Me$_3$Si, s); ^{13}C NMR δ 136.11, 135.47, 133.13, 132.57, 129.34, 128.85, 111.71, 111.32, 38.14, 36.26, 22.38, 21.05, 20.76, 17.87, 17.54, 17.16, 14.36, 14.14, –0.27, –0.30; MS m/e 196 (M^+, 6), 167 (1), 139 (1), 107 (1), 93 (3), 85 (1), 79 (1), 73 (100).

2-[(*Z*)-4-Butyl-3,5-hexadienyl]cyclohexanone (31a): IR (neat) 1700 (s), 1630 (w), 1585 (m), 1435 (s), 1365 (m), 1330 (w), 1305 (m), 1220 (m), 1190 (m), 1120 (s), 1070 (w), 980 (s), 890 (s), 825 (w), 710 (w) cm^{-1}; ^1H NMR δ 6.61 (1 H, ddd, J = 17.6, 11.0, and 0.9 Hz), 5.31 (1 H, t, J = 7 Hz), 5.19 (1 H, d, J = 17.4 Hz),

(32) Häussinger, P.; Kresze, G. *Tetrahedron* **1978**, *34*, 689–696.

5.04 (1 H, dt, J = 11.2 and 1.5 Hz), 2.4–1.9 (9 H, m), 1.84 (2 H, br m), 1.63 (2 H, br m), 1.4–1.1 (6 H, br m), 0.88 (3 H, m); ^{13}C NMR δ 213.10, 137.10, 132.74, 129.71, 113.08, 49.93, 42.04, 33.97, 32.96, 31.02, 29.54, 28.02, 24.95, 24.85, 22.62, 13.94.

2-[(*E*)-4-[(Trimethylsilyl)methyl]-3,5-hexadienyl]cyclohexanone (31b): IR (neat) 1710 (s), 1630 (w), 1595 (w), 1445 (m), 1245 (s), 1155 (w), 1120 (w), 1080 (w), 1030 (w), 1010 (w), 980 (w), 895 (m), 840 (s), 695 (m) cm^{-1}; ^{1}H NMR δ 6.68 (1 H, ddd, J = 17.4, 10.9, and 0.9 Hz), 5.14 (1 H, t, J = 7 Hz), 5.10 (1 H, d, J = 17 Hz), 5.04 (1 H, d, J = 11 Hz), 2.4–2.2 (3 H, m), 2.2–2.1 (2 H, m), 2.0 (2 H, br), 1.8 (2 H, m), 1.62 (2 H, br), 1.61 (2 H, s), 1.37 (1 H, m), 1.2 (1 H, m), –0.04 (9 H, s); ^{13}C NMR δ 213.14, 134.58, 133.49, 128.32, 113.78, 49.86, 42.12, 34.06, 29.81, 28.07, 25.04, 24.94, 22.35, –1.00; MS m/e 264 (M$^+$, 11), 249 (2), 235 (2), 207 (3), 196 (2), 195 (3), 183 (7), 170 (6), 169 (10), 166 (20), 155 (6), 145 (6), 93 (8), 92 (15), 90 (8), 79 (39), 73 (100).

Methyl (*E*)-7-methyl-6,8-nonadienoate (33a): IR (neat) 1740 (s), 1640 (w), 1610 (w), 1440 (m), 1370 (m), 1210 (m), 1180 (m), 1080 (m), 990 (m), 900 (m), 860 (w) cm^{-1}; ^{1}H NMR δ 6.34 (1 H, dd, J = 17.3 and 10.7 Hz), 5.45 (1 H, t, J = 7 Hz), 5.06 (1 H, d, J = 17.4 Hz), 4.91 (1 H, d, J = 10.8 Hz), 3.65 (3 H, s), 2.30 (2 H, t), 2.14 (2 H, q), 1.71 (3 H, s), 1.63 (2 H, m), 1.40 (2 H, m); ^{13}C NMR δ 174.02, 141.47, 134.27, 132.52, 110.54, 51.39, 33.94, 28.94, 27.79, 24.61, 11.63.

(*E*)-7-Methyl-6,8-nonadienoic acid (34): IR (neat) 3500–2500 (br s), 1700 (s), 1630 (w), 1590 (w), 1400 (s), 1280 (s), 1230 (s), 1060 (w), 980 (m), 880 (s), 830 (m), 740 (w) cm^{-1}; ^{1}H NMR δ 10 (OH, br), 6.36 (1 H, dd, J = 17.6 and 10.6 Hz), 5.47 (1 H, t, J = 7 Hz), 5.08 (1 H, d, J = 17.2 Hz), 4.93 (1 H, d, J = 10.6 Hz), 2.36 (2 H, t, J = 7.3 Hz), 2.16 (2 H, q, J = 7.3 Hz), 1.73 (3 H, s), 1.66 (2 H, quintet), 1.44 (2 H, quintet); ^{13}C NMR δ 179.84, 141.47, 134.37, 132.44, 110.65, 33.93, 28.87, 27.80, 24.35, 11.68.

Methyl (*E*)-7-butyl-6,8-nonadienoate (33b): IR (neat) 1735 (s), 1630 (w), 1600 (w), 1450 (m), 1430 (m), 1370 (w), 1200 (m), 1170 (m), 1110 (w), 1085 (m), 990 (m), 890 (m), 850 (m) cm^{-1}; ^{1}H NMR δ 6.23 (1 H, dd, J = 17.4 and 10.8 Hz), 5.40 (1 H, t, J = 7.2 Hz), 5.08 (1 H, d, J = 17.6 Hz), 4.91 (1 H, d, J = 10.8 Hz), 3.65 (3 H, s), 2.31 (2 H, t), 2.19 (2 H, t), 2.12 (2 H, q), 1.65 (2 H, m), 1.45–1.25 (6 H, m), 0.90 (3 H, t); ^{13}C NMR δ 174.04, 140.36, 139.06, 132.41, 110.38, 51.43, 33.98, 31.19, 29.14, 27.76, 25.99, 24.71, 23.02, 14.00.

Oxidation of Allylboranes. The following procedure for the oxidation of allylborane 7 is representative. To 5 mL of 6 N NaOH and 5 mL of 30% H_2O_2 was added via cannula 5.0 mmol of 7 in THF. After 2 h of stirring, the reaction mixture was heated at 50 °C for 30 min to ensure complete oxidation. The organic layer was concentrated, and the residue was column chromatographed on silica gel, eluting with hexane followed by a mixture of hexane and ethyl acetate (10:1) solution to afford 0.52 g (72%) of (*E*)-3-(trimethylsilyl)-2-buten-1-ol (17)[8a] as a colorless liquid: IR (neat) 3300 (OH, br), 1620 (w), 1440 (m), 1400 (m), 1360 (m), 1250 (s), 1140 (m), 1070 (s), 1010 (s), 950 (m), 830 (s), 750 (s), 690 (m), 620 (m) cm^{-1}; ^{1}H NMR δ 5.86 (1 H, tq, J = 6 and 1.7 Hz), 4.25 (2 H, d, J = 5.9 Hz), 1.69 (3 H, dt, J = 1.7 and 0.9 Hz), 1.66 (OH, br), 0.05 (9 H, s); ^{13}C NMR δ 139.31, 137.56, 59.52, 14.58, –2.33. The ^{1}H NMR spectrum is identical with those of the reported data.[8a,b] The Z isomer[8c] was not detected by the ^{1}H spectrum (<1%).

Oxidation of 8. Oxidation of 8 (2.5 mmol) was carried out as described for 7. Purification by column chromatography afforded 0.32 g (69%) of 3-(trimethylsilyl)-2-hepten-1-ol (18) (*E*:*Z* = 98:2) as a colorless liquid: IR (neat) 3300 (OH, br), 1610 (w), 1450 (m), 1410 (w), 1380 (w), 1245 (s), 1030 (m), 835 (s), 750 (m), 690 (m) cm^{-1}; ^{1}H NMR δ (*E* isomer) 5.84 (1 H, t, J = 6.0 Hz), 4.20 (2 H, d, J = 6.0 Hz), 2.44 (1 H, br, OH), 2.08 (2 H, t, J = 7.5 Hz), 1.25 (4 H, br m), 0.86 (3 H, t), 0.04 (3 H, s); ^{13}C NMR (*E* isomer) δ 143.94, 138.42, 59.27, 32.57, 29.70, 22.93, 13.84, –1.44. The ^{1}H NMR chemical shifts of the vinylic hydrogen and the allylic hydrogens on C(1) of the minor isomer are identical with those of the Z isomer.[8c]

Oxidation of 9. Oxidation of 9 (4.2 mmol) afforded 0.70 g (77%) of (*E*)-3,4-bis(trimethylsilyl)-2-buten-1-ol (19) as a colorless liquid: bp 62 °C (0.02 Torr); IR (neat) 3300 (OH, br), 1410 (w), 1250 (s), 1180 (w), 1150 (w), 1020 (m), 840 (s), 750 (m), 690 (m) cm^{-1}; ^{1}H NMR δ 5.76 (1 H, tt, J = 6.1 and 1.2 Hz), 4.15 (2 H, d, J = 6.1 Hz), 1.68 (2 H, d, J = 1 Hz), 1.58 (1 H, br, OH), 0.06 (9 H, s), 0.00 (9 H, s); ^{13}C NMR δ 141.60, 135.46, 60.22, 20.75, –0.40, –1.14. The assignment of the geometry of the double bond was based on the nuclear Overhauser effect. On irradiation of the methyl groups (δ 0.06) attached to the silicon at C(3), the vinylic hydrogen showed a 10% increase in integrated intensity, and the allylic hyrogens on C(1) were not affected. On the other hand, irradiation of the methyl groups at δ 0.00 did not affect the integrated intensities of both the vinylic hydrogen and the allylic hydrogens on C(1). The Z isomer was not detected in the ^{1}H NMR spectrum (<1%).

Oxidation of 10. Oxidation of 10 (2.0 mmol) afforded 0.23 g (55%) of 3-(trimethylsilyl)-3-phenyl-2-propen-1-ol (20) (*E*:*Z* = 98:2) as a colorless liquid: IR (neat) 3300 (OH, br), 1670 (w), 1590 (w), 1490 (m), 1440 (m), 1400 (m), 1250 (s), 1190 (m), 1070 (m), 1020 (s), 970 (m), 930 (s), 895 (s), 840 (s), 770 (s), 750 (s), 705 (s), 620 (s) cm^{-1}; ^{1}H NMR (*E* isomer) δ 7.29 (2 H, tm), 7.19 (1 H, tm), 6.92 (2 H, dm), 6.13 (1 H, t, J = 6.1 Hz), 4.01 (2 H, d, J = 6.1 Hz), 1.7 (1 H, br, OH), 0.07 (9 H, s); ^{13}C NMR (*E* isomer) δ 147.38, 141.51, 139.26, 128.12, 127.28, 125.78, 60.81, –1.74. The ^{1}H NMR spectrum of the minor isomer was identical with that of (*Z*)-3-(trimethylsilyl)-3-phenyl-2-propen-1-ol independently synthesized from 3-phenyl-2-propyn-1-ol. The following procedure was utilized for the synthesis of (*Z*)-3-(trimethylsilyl)-3-phenyl-2-propen-1-ol. To a solution of Red-Al (3.4 M in toluene, 8.2 mL, 27.9 mmol) in 15 mL of Et_2O at 0 °C was added dropwise a solution of 3-phenyl-2-propyn-1-ol (2.09 g, 15.9 mmol) in 15 mL of Et_2O.[9a,b] The mixture was stirred at 0 °C for 2 h before 3 mL of anhydrous ethyl acetate was introduced. The reaction mixture was then cooled to –78 °C and treated dropwise with a solution of iodine (5.0 g, 19.7 mmol) in 15 mL of THF until the iodine color persisted. The mixture was warmed to room temperature followed by the usual workup to afford 3.8 g (92%) of (*Z*)-3-iodo-3-phenyl-2-propen-1-ol as a colorless liquid: ^{1}H NMR δ 7.49 (2 H, m), 7.29 (3 H, m), 6.25 (1 H, t, J = 5.6 Hz), 4.38 (2 H, d, J = 5.7 Hz); ^{13}C NMR δ 142.17, 137.00, 128.70, 128.42, 128.30, 105.06, 68.27.

To a solution of 2.73 g of (*Z*)-3-iodo-3-phenyl-2-propen-1-ol (10.5 mmol) in 20 mL of THF at 0 °C were introduced 1.8 mL of Et_3N (12.6 mmol) and 1.5 mL of Me_3SiCl (11.6 mmol). After 1 h of stirring at room temperature, 25 mL of Et_2O was introduced. The reaction mixture was then washed with 20 mL of aqueous $NaHCO_3$ solution. The organic layer was passed through a short silica gel column to afford 3.33 g (95%) of the corresponding trimethylsilyl ether: ^{1}H NMR δ 7.48–7.42 (2 H, m), 7.32–7.20 (3 H, m), 6.18 (1 H, t, J = 5.2 Hz), 4.36 (2 H, d, J = 5.1 Hz), 0.18 (9 H, s); ^{13}C NMR δ 142.20, 138.04, 128.44, 128.36, 128.18, 102.67, 68.79, –0.34.

To a solution of 1.6 g of the above trimethylsilyl ether (4.8 mmol) in 10 mL of THF at –78 °C was added dropwise 5.8 mL of a 1.7 M solution of *tert*-butyllithium (9.9 mmol) in pentane. The reaction mixture was then allowed to warm to room temperature before 5 mL of a 5% aqueous $NaHCO_3$ solution was introduced. The organic layer was concentrated, and the residue was chromatographed on silica gel, eluting with 20% Et_2O in hexane followed by simple distillation at reduced pressure (0.05 Torr) to afford 0.68 g (69%) of (*Z*)-3-(trimethylsilyl)-3-phenyl-2-propen-1-ol as a colorless liquid:[9c] IR (neat) 3300 (OH, br), 1595 (w), 1485 (m), 1440 (m), 1355 (w), 1250 (s), 1100 (w), 1070 (w), 1030 (s), 910 (m), 880 (s), 840 (s), 765 (s), 700 (s), 620 (s) cm^{-1}; ^{1}H NMR δ 7.3–7.1 (3 H, m), 7.05–6.95 (2 H, dm), 6.22 (1 H, t, J = 6.8 Hz), 4.34 (2 H, d, J = 6.6 Hz), 2.0 (1 H, br, OH), 0.14 (9 H, s); ^{13}C NMR δ 146.60, 146.10, 143.82, 127.84, 127.09, 125.73, 62.06, 0.67. Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 69.41; H, 8.57.

Oxidation of 11. Oxidation of 11 (2.8 mmol) afforded 0.32 g (66%) of 4-methyl-3-(trimethylsilyl)-2-penten-1-ol (21) (*E*:*Z* = 92:8) as a colorless liquid: IR (neat) 3300 (OH, br), 1450 (m), 1400 (w), 1360 (m), 1245 (s), 1170 (w), 1150 (w), 1100 (w), 1030 (s), 950 (m), 880 (s), 840 (s), 750 (s), 690 (m), 620 (m) cm^{-1}; ^{1}H NMR (*E* isomer) δ 5.78 (1 H, t, J = 5.7 Hz), 4.27 (2 H, d, J = 5.7 Hz), 2.74 (1 H, septet, J = 7 Hz), 2.04 (1 H, br, OH), 1.03 (6 H, d, J = 7.2 Hz), 0.10 (9 H, s); ^{13}C NMR (*E* isomer) δ 149.79, 138.16, 59.81, 30.86, 22.81, 0.39. The ^{1}H and ^{13}C NMR spectra of the minor isomer were found to be identical with those of (*Z*)-4-methyl-3-(trimethylsilyl)-2-penten-1-ol independently synthesized from 4-methyl-2-pentyn-1-ol (overall yield 35%) by a procedure reported previously.[3b] Z isomer: IR (neat) 3300 (OH, br), 1610 (w), 1460 (m), 1405 (m), 1380 (m), 1360 (m), 1250 (s), 1175 (w), 1105 (w), 1025 (s), 975 (m), 860 (s), 835 (s), 755 (s), 685 (m) cm^{-1}; ^{1}H

NMR δ 6.14 (1 H, td, J = 7.0 and 1.1 Hz), 4.21 (2 H, d, J = 7.0 Hz), 2.43 (1 H, septet, J = 6.8 Hz), 0.99 (6 H, d, J = 6.8 Hz), 0.15 (9 H, s); ^{13}C NMR δ 150.54, 136.33, 62.34, 32.59, 23.08, 0.62.

Oxidation of 12. Oxidation of **12** (4.2 mmol) afforded 0.39 g (50% of 4,4-dimethyl-3-(trimethylsilyl)-2-penten-1-ol (**22**) (*E*:*Z* = 42:58) as a colorless liquid: IR (neat) 3300 (OH, br), 1590 (w), 1460 (m), 1410 (m), 1390 (m), 1360 (s), 1250 (s), 1220 (m), 1200 (m), 1030 (s), 980 (m), 930 (m), 830 (s), 760 (m), 680 (m). *E* isomer (minor): ^{1}H NMR δ 5.76 (1 H, t, J = 5.2 Hz), 4.36 (2 H, d, J = 5.0 Hz), 2.93 (1 H, br, OH), 1.10 (9 H, s), 0.11 (9 H, s); ^{13}C NMR δ 150.76, 140.89, 61.59, 36.68, 31.55, 1.89. *Z* isomer (major): ^{1}H NMR δ 6.08 (1 H, t, J = 6.7 Hz), 4.22 (2 H, d, J = 6.4 Hz), 2.59 (1 H, br, OH), 1.05 (9 H, s), 0.19 (9 H, s); ^{13}C NMR δ 151.93, 136.50, 61.91, 37.75, 30.22, 3.34. The ^{1}H and ^{13}C NMR spectra of the major isomer were found to be identical with those of (*Z*)-4,4-dimethyl-3-(trimethylsilyl)-2-penten-1-ol (crystalline solid, mp 68.5–69.5 °C, overall yield 25%) independently synthesized from 4,4-dimethyl-2-pentyn-1-ol by a procedure reported previously.[3b]

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Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra of **16a**, **15b**, **16b**, and all new compounds (78 pages). Ordering information is given on any current masthead page.

Palladium-Catalyzed Cyclocarbonylation of 3-(Heteroaryl)allyl Acetates[1]

Masakazu Iwasaki, Yoshihiro Kobayashi, Ji-Ping Li, Hiroyuki Matsuzaka, Youichi Ishii, and Masanobu Hidai*

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

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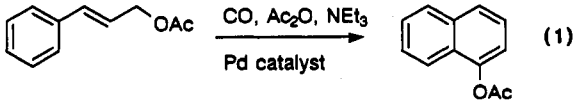
Acetoxybenzofurans, acetoxybenzothiophenes, acetoxyindoles, and acetoxycarbazoles were obtained in high yields by cyclocarbonylation of 3-furyl-, 3-thienyl-, 3-pyrrolyl-, and 3-indolylallyl acetates, respectively, in the presence of Ac_2O, NEt_3, and a catalytic amount of $PdCl_2(PPh_3)_2$ at 130–170 °C under 50–70 atm of CO. 3-(3-Furyl)allyl and 3-(3-thienyl)allyl acetates cyclized selectively at the 2-position of the heterocyclic nucleus to give 7-acetoxybenzofuran and 7-acetoxybenzothiophene, respectively. The synthetic utility of the reaction was demonstrated by the synthesis of cannabifuran from isothymol.

Introduction

Fused heteroaromatic systems, such as benzofurans, indoles, and carbazoles, are among the most attractive targets of organic synthesis because of their wide occurrence in natural products. Especially desirable is a synthetic route to fused-ring heteroaromatics with functional groups at specific positions. The catalytic cyclocarbonylation of monocyclic aromatic heterocycles shows promise as a useful reaction for the synthesis of such functionalized fused-ring heteroaromatics.

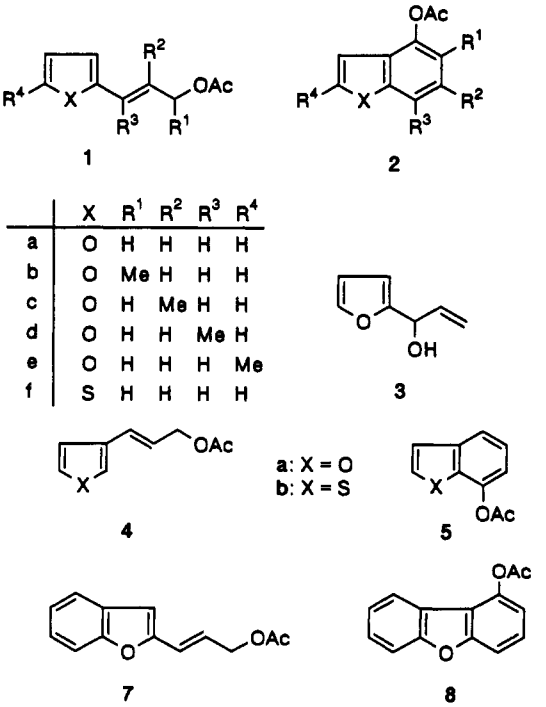
Although there are reports of cyclcarbonylations leading to anthraquinone,[2] indenones,[3] and indanones,[4] no examples of the cyclocarbonylation of aromatic heterocycles have appeared in the literature. Earlier, we reported[5] a novel palladium-catalyzed cyclocarbonylation of cinnamyl acetates, which involved an intramolecular carbonylation of the phenyl ring, to give naphthyl acetates (eq 1). We



(1)

have also applied cyclocarbonylation to the selective synthesis of 1- and 4-acetoxyphenanthrenes.[6] The reaction is synthetically valuable because easily accessible 3-arylallyl acetates are used as starting materials. Extensive investigation of the reaction has led to a novel synthetic method for fused-ring heteroaromatic compounds with acetoxy

Chart I



(1) Construction of Polycyclic Compounds by Cyclocarbonylation. 6. Part 5: See ref 7.

(2) Arzoumanidis, G. G.; Rauch, F. C. *J. Mol. Catal.* **1980**, *9*, 335.

(3) (a) Kim, P. J.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 2022. (b) Hong, P.; Cho, B.; Yamazaki, H. *Chem. Lett.* **1979**, 339.

(4) (a) Bruson, H. A.; Plant, H. L. *J. Org. Chem.* **1967**, *32*, 3356. (b) Doyama, K.; Fujiwara, K.; Joh, T.; Maeshima, K.; Takahashi, S. *Chem. Lett.* **1988**, 901.

(5) (a) Matsuzaka, H.; Hiroe, Y.; Iwasaki, M.; Ishii, Y.; Koyasu, Y.; Hidai, M. *Chem. Lett.* **1988**, 377. (b) Matsuzaka, H.; Hiroe, Y.; Iwasaki, M.; Ishii, Y.; Koyasu, Y.; Hidai, M. *J. Org. Chem.* **1988**, *53*, 3832. (c) Koyasu, Y.; Matsuzaka, H.; Hiroe, Y.; Uchida, Y.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1987**, 575.

(6) Iwasaki, M.; Matsuzaka, H.; Hiroe, Y.; Ishii, Y.; Hidai, M. *Chem. Lett.* **1988**, 1159.

0022-3263/91/1956-1922$02.50/0