A Versatile Synthesis of 1,4-Dienes: Use of Vinyl Ethers as Vinyl Cation Equivalents☆

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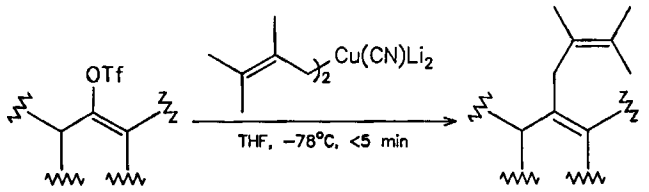
The α,β-dibromo ethers **2**, in situ generated from the vinyl ethers **1** and bromine, react with the allylsilanes **3** in the presence of $ZnCl_2$ to give the β-bromo ethers **4**. Treatment of **4** with Na in diethyl ether yields 1,4-dienes **5** in 62–79% overall yield.

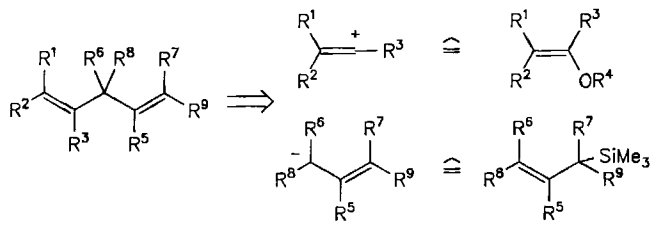
Most syntheses of 1,4-dienes proceed by combination of vinylic nucleophiles with allylic electrophiles[1], and examples for the coupling of a vinylic electrophile with an allylic nucleophile are rare[1]. A general method for the synthesis of 1,4-dienes using the latter approach has recently been described by Lipshutz (Scheme 1)[2].

Scheme 1



We now describe another example for constructing 1,4-dienes from vinyl cation and allyl anion equivalents, where the readily available vinyl ethers are used as vinyl cation equivalents (Scheme 2).

Scheme 2

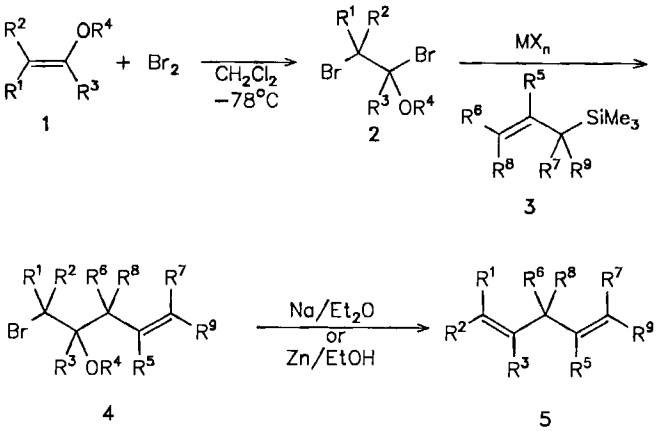


For this purpose, the reaction sequence depicted in Scheme 3 has been elaborated. A comparison of structures **1** and **5** shows that, overall, the alkoxy group of vinyl ethers is replaced by an allylic group.

Formation of the β-Bromo Ethers 4

In view of the high tendency of vinyl ethers to undergo cationic polymerization, the 1,2-dibromo ethers **2** have been prepared by dropwise addition of the vinyl ethers **1** to solutions of bromine in CH_2Cl_2 at −78 °C. Even under these conditions a small excess of **1** over bromine is usually needed to achieve complete decolorization of the bromine solution (see Experimental). The highly reactive and ***presumably toxic*** dibromo ethers **2** have not been isolated, and the β-bromo ethers **4** have been produced in a one-pot reaction by adding $ZnCl_2-Et_2O$[3] and the allylsilanes **3** to the dichloromethane solutions obtained by bromination of the vinyl ethers[4]. Compounds **4** have either been purified by distillation or immediately converted into the 1,4-dienes **5**.

Scheme 3



All combinations of enol ethers and allylsilanes examined in this work gave the β-bromo ethers **4** in good yield. Contaminations observed in some runs were due to the use of moist bromine, leading to HBr adducts of the vinyl ethers, which then reacted with the allylsilanes **3** to give debrominated analogs of **4** (e.g. **7**). As the stereochemistry of the intermediate bromo ethers **4** is usually not important for the structure of the elimination products **5**, the diastereoselectivities of the C–C bond-forming reactions have generally not been investigated. Only in the case of **4c**, a ^{13}C-NMR spectrum has been taken, which showed the highly selective formation of one diastereomer (≈95:5) from a 2:1 mixture of diastereomeric dibromo ethers **2c**.

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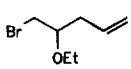
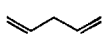
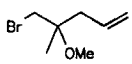
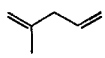
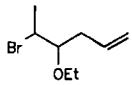
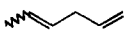
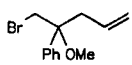
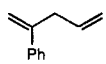
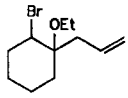
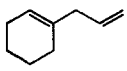
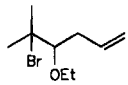
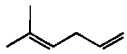
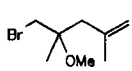
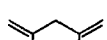
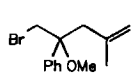
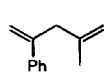
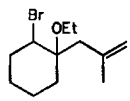
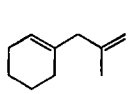
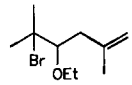
Elimination Reactions

The production of alkenes by Zn-promoted elimination of halogen and alkoxyl from β-halogeno ethers has long been known[5]. The reaction conditions were optimized for the conversion **4d** → **5d**, and it was found that a mixture of **4d** and 5 equivalents of zinc powder in ethanol or methanol had to be refluxed for approximately 20 hours to achieve complete consumption of the bromo ether. A slight retardation of the elimination was observed, when 4 mol-% of $ZnCl_2$ was added to the reaction mixture.

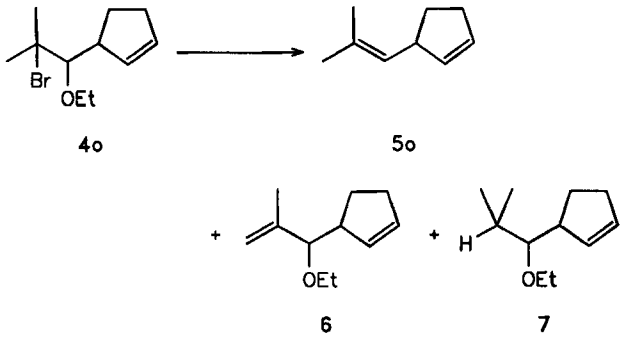
Table 1. 1,4-Dienes **5** from vinyl ethers **1** and allylsilanes **3**

Vinyl Ethers	Allylsilanes	β-Bromo ethers (% Yield)	1,4-Dienes	(% Yield Zn/EtOH[a]	Na/Et_2O[a])
 **1a**	 **3a**	 **4a** (87)	 **5a**		
 **1b**	 **3a**	 **4b** (73)	 **5b**		
 **1c**	 **3a**	 **4c** (92)	 **5c**		
 **1d**	 **3a**	 **4d** (92)[b]	 **5d**	(79)	
 **1e**	 **3a**	 **4e** (84)	 **5e**	(40)	
 **1f**	 **3a**	 **4f** (81)	 **5f**		
 **1b**	 **3b**	 **4g** (86)	 **5g**	(38)[c]	
 **1d**	**3b**	 **4h** (97)[b]	 **5h**	(75)	(65)
 **1e**	**3b**	 **4i** (68)[b]	 **5i**	(61)	(74)
 **1f**	**3b**	 **4j** (92)[b]	 **5j**	(20)	(72)
1a	**3c**	**4k**	**5k**		(62)
1c	**3d**	**4l** (99)[b]	**5l**		(64)
1d	**3e**	**4m** (92)[b]	**5m**	(75)	
1e	**3e**	**4n** (88)[b]	**5n**		(54)
1f	**3e**	**4o** (88)[b]	**5o**	(30)	(67)

[a] Yield with respect to vinyl ethers **1** and allylsilanes **3**. — [b] Yield of crude material. — [c] Ref.[10].

While the elimination with zinc in alcohols gave satisfactory results in several cases (Table 1), there were systems, where generally high amounts of side products were observed under these conditions. Treatment of **4o** with zinc dust (Riedel-de Haën) in ethanol, for example, gave **5o**, **6**, and **7** (Scheme 4) in a 58:33:9 ratio (GC), and zinc powder (Merck) in ethanol yielded these compounds in a 72:22:6 ratio. Heating of **4o** with a Zn/Cu couple (Merck) even led to the predominant formation of **6** (**5o**:**6**:**7** = 38:46:16). While no reaction was observed when **4o** was treated with magnesium turnings in diethyl ether, the analogous treatment with sodium wire led to the selective formation of compound **5o**[6].

Scheme 4

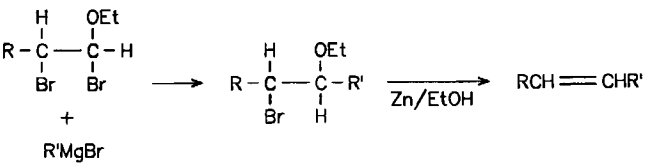


As this method gave good yields of 1,4-dienes in all cases examined, the elimination with Na in Et_2O is the method of choice for further applications.

Conclusion

Scheme 3 provides a straightforward synthesis for 1,4-dienes with variable substitution pattern. This method may be considered as a variant of the Boord olefin synthesis (Scheme 5)[5,7], which has also been employed for the synthesis of 1,4-dienes by using allylic Grignard reagents[8]. As unsymmetrical allylmagnesium halides often do not react regioselectively, the advantage of the method presented in this article is not only the higher overall yield but also the greater regioselectivity of the C–C bond-forming reaction.

Scheme 5



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Experimental

^{1}H NMR: EM 390 (Varian). – ^{13}C NMR: XL 200 (Varian). – MS: 70–250 E (VG-Instruments).

The enol ethers were commercially available (**1a–c**), or were synthesized from the corresponding acetals by H_3PO_4-catalyzed alcohol elimination using literature procedures (**1d–f**)[9]. The allylsilanes **3b** and **3e** were obtained by magnesium-promoted coupling of the corresponding allyl chlorides with chlorotrimethylsilane[10,11], **3c** was prepared by photochemically induced hydrosilation of 2,3-dimethyl-1,3-butadiene in the presence of $Cr(CO)_6$[12] and **3d** from (trimethylsilyl)methylmagnesium chloride and 1-(trimethylsiloxy)-1-cyclohexene in the presence of catalytic amounts of nickel acetylacetonate[13].

Typical Procedure for the Synthesis of the β-Bromo Ethers **4**: Bromine (1.60 g, 10.0 mmol) was dissolved in CH_2Cl_2 (20 ml) in a 100-ml flask and the solution cooled at –78 °C. A solution of the enol ether **1e** (1.39 g, 11.0 mmol) in CH_2Cl_2 (20 ml) was added dropwise with stirring, leading to complete decolorization of the solution. Allylsilane **3a** (1.26 g, 11.0 mmol) and $ZnCl_2$–Et_2O [4.8 mmol; 2.5 ml of a solution obtained by dissolving $ZnCl_2$ (50 g) in diethyl ether (60 ml) and dichloromethane (120 ml)][3] were added, and the mixture was kept at –78 °C for 2 h. The solution was washed with two 35-ml portions of 25% aqueous NH_4Cl and dried with $MgSO_4$. After evaporation of the solvent, spectroscopically pure *1-allyl-2-bromo-1-ethoxycyclohexane* (**4e**) was obtained in 84% yield (2.29 g). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.05–2.78 (m, 13H), 3.20–3.70 (m, 2H, OCH_2CH_3), 4.10 (m_c, 1H, CHBr), 5.0–5.4 (m, 2H, $=CH_2$), 5.73 (m_c, 1H, CH=).

Note: This procedure is recommended for all compounds **4**, though in the early phase of this project different amounts of the reactants have been used (see below).

5-Bromo-4-ethoxy-1-pentene (**4a**) was obtained in 87% yield (1.17 g) from Br_2 (1.12 g, 7.01 mmol), **1a** (500 mg, 6.93 mmol), $ZnCl_2$–Et_2O (1.75 ml, 3.36 mmol), and **3a** (1.20 g, 10.5 mmol) after a reaction time of 15 h; b.p. 40–45 °C (bath)/2–5 mbar [ref.[14] 81.8–84.0 °C (33 mbar)]. – ^{1}H NMR (CCl_4): δ = 1.20 (t, *J* = 6.0 Hz, 3H, OCH_2CH_3), 2.37 (m_c, 2H, 3-H), 3.23–3.75 (m, 5H, 4-H, 5-H, OCH_2CH_3), 4.97–5.27 (m, 2H, 1-H), 5.80 (m_c, 1H, 2-H).

5-Bromo-4-methoxy-4-methyl-1-pentene (**4b**): Vinyl ether **1b** (720 mg, 10.0 mmol), Br_2 (1.60 g, 10.0 mmol), $ZnCl_2$–Et_2O (2.5 ml, 4.84 mmol), and **3a** (1.71 g, 15.0 mmol) gave **4b** (1.40 g, 73%) with b.p. 25–30 °C (bath)/0.4 mbar (reaction time 15 h). – ^{1}H NMR (CCl_4): δ = 1.22 (s, 3H, CH_3), 2.35 (br. d, *J* = 6 Hz, 2H, 3-H), 3.21 (s, 3H, OCH_3), 3.27 (s, 2H, 5-H), 4.93–5.22 (m, 2H, 1-H), 5.47–5.97 (m, 1H, 2-H).

5-Bromo-4-ethoxy-1-hexene (**4c**): The dibromo ether prepared from Br_2 (1.12 g, 7.01 mmol) and (*E,Z*)-**1c** (600 mg, 7.00 mmol, *E*-**1c**:*Z*-**1c** = 30:70) reacted within 15 h with **3a** (1.20 g, 10.5 mmol) in the presence of $ZnCl_2$–Et_2O (1.8 ml, 3.46 mmol) to give **4c** (1.33 g, 92%) with b.p. 40–45 °C (bath)/4 mbar. – ^{1}H NMR ($CDCl_3$): δ = 1.21 (t, *J* = 7.0 Hz, 3H, OCH_2CH_3), 1.70 (d, *J* = 6.8 Hz, 3H, 6-H), 2.42 (br. t, *J* = 6.2 Hz, 2H, 3-H), 3.41 (q, *J* = 5.4 Hz, 1H, 4-H), 3.63 (m_c, 2H, OCH_2CH_3), 4.14 (qd, *J* = 6.8/5.4 Hz, 1H, 5-H), 5.06–5.20 (m, 2H, 1-H), 5.85 (m_c, 1H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 15.48 (q, OCH_2CH_3), 21.35 (q, C-6), 36.49 (t, C-3), 51.31 (d, C-5), 66.52 (t, OCH_2CH_3), 83.02 (d, C-4), 117.58 (t, C-1), 134.13 (d, C-2). – The ^{13}C-NMR spectrum indicates a 95:5 ratio of diastereomers. – MS (70 eV): *m/z* (%) = 165, 167 (94, 92) [$M^+ - C_3H_5$], 137, 139 (84, 82) [$M^+ - C_3H_4 - C_2H_4$], 57 (100) [$M^+ - C_3H_5 - C_2H_4 - HBr$].

5-Bromo-4-methoxy-4-phenyl-1-pentene (**4d**): 5.00 g of a 83:17 mixture of **1d** and acetophenone dimethyl acetal (total 37.0 mmol), bromine (5.92 g, 37.0 mmol), $ZnCl_2$–Et_2O (9.3 ml, 17.9 mmol), and **3a** (6.30 g, 55.1 mmol) gave 8.67 g (92%) of spectroscopically pure

4d. – ^{1}H NMR ($CDCl_3$): δ = 2.74 (br. d, J = 6.5 Hz, 2H, 3-H), 3.10 (s, 3H, OCH_3), 3.69 (s, 2H, 5-H), 4.93–5.28 (m, 2H, 1-H), 5.29–5.82 (m, 1H, 2-H), 7.28 (m_c, 5H, Ph).

4e: See typical procedure.

5-Bromo-4-ethoxy-5-methyl-1-hexene (**4f**) was prepared in 81% yield (3.92 g) from **1f** (2.20 g, 22.0 mmol), bromine (3.20 g, 20.0 mmol), $ZnCl_2$–Et_2O (5.0 ml, 9.60 mmol), and **3a** (2.51 g, 22.0 mmol): b.p. 62–73°C/2–5 mbar. – ^{1}H NMR ($CDCl_3$): δ = 1.17 (t, J = 6.0 Hz, 3H, OCH_2CH_3), 1.72, 1.77 (2 s, 6H, 5-CH_3, 6-H), 1.03–2.83 (m, 2H, 3-H), 3.30 (m_c, 1H, 4-H), 3.63 (q, J = 6.0 Hz, 2H, OCH_2CH_3), 4.87–5.27 (m, 2H, 1-H), 5.60–6.20 (m, 1H, 2-H).

5-Bromo-4-methoxy-2,4-dimethyl-1-pentene (**4g**): Vinyl ether **1b** (1.52 g, 21.1 mmol), bromine (3.07 g, 19.2 mmol), $ZnCl_2$–Et_2O (4.8 ml, 9.22 mmol), and **3b** (2.70 g, 21.0 mmol) gave 3.77 g (86%) of **4g**: B.p. 50–70°C (bath)/1 mbar (ref.[10] 30–40°C (bath)/0.02 mbar). – ^{1}H NMR ($CDCl_3$): δ = 1.27 (s, 3H, 4-CH_3), 1.80 (br. s, 3H, 2-CH_3), 2.40 (br. s, 2H, 3-H), 3.23 (s, 3H, OCH_3), 3.40 (s, 2H, 5-H), 4.80, 4.90 (2 m_c, 2H, 1-H).

5-Bromo-4-methoxy-2-methyl-4-phenyl-1-pentene (**4h**): 1.47 g of a 83:17 mixture of **1d** and acetophenone dimethyl acetal (total 11.0 mmol), bromine (1.60 g, 10.0 mmol), $ZnCl_2$–Et_2O (2.5 ml, 4.84 mmol), and **3b** (1.41 g, 11.0 mmol) gave **4h** (2.86 g, 97%) as an orange, spectroscopically pure liquid. – ^{1}H NMR (CCl_4): δ = 1.36 (s, 3H, 2-CH_3), 2.50, 2.75 (AB system, J = 13.5 Hz, 2H, 3-H), 3.08 (s, 3H, OCH_3), 3.72, 3.90 (AB system, J = 9.0 Hz, 2H, $BrCH_2$), 4.73 (m_c, 2H, C=CH_2), 7.28 (m_c, 5H, Ph).

2-Bromo-1-ethoxy-1-(2-methylallyl)cyclohexane (**4i**): Compound **1e** (2.77 g, 22.0 mmol), bromine (3.20 g, 20.0 mmol), $ZnCl_2$–Et_2O (5.0 ml, 9.6 mmol), and **3b** (2.82 g, 22.0 mmol) gave 3.93 g (68%) of crude **4i**. – ^{1}H NMR ($CDCl_3$): δ = 1.05–2.68 (m, 16H, 3-, 4-, 5-, 6-H, OCH_2CH_3, CH_3, =CCH_2), 3.53 (m_c, 2H, OCH_2CH_3), 4.26 (m_c, 1H, 2-H), 4.92 (br. s, 2H, C=CH_2).

5-Bromo-4-ethoxy-2,5-dimethyl-1-hexene (**4j**) was obtained in 92% yield (1.19 g) from **1f** (550 mg, 5.49 mmol), bromine (800 mg, 5.00 mmol), $ZnCl_2$–Et_2O (1.3 ml, 2.52 mmol), and **3b** (705 mg, 5.50 mmol). – ^{1}H NMR ($CDCl_3$): δ = 1.18 (t, J = 6 Hz, 3H, OCH_2CH_3), 1.71, 1.78, 1.85 [3 s, 9H, $BrC(CH_3)_2$, 2-CH_3], 2.02–2.70 (m, 2H, 3-H), 3.31–3.84 (m, 3H, OCH_2CH_3, 4-H), 4.83 (br. s, 2H, C=CH_2).

5-Bromo-4-ethoxy-2,3,3-trimethyl-1-pentene (**4k**): Vinyl ether **1a** (1.59 g, 22.0 mmol), bromine (3.20 g, 20.0 mmol), $ZnCl_2$–Et_2O (5.0 ml, 9.60 mmol), and **3c** (4.37 g, 22.0 mmol) gave 8.52 g of a mixture of **4k** and of hexaethyldisiloxane which was not separated but subjected to treatment with sodium (see below). The spectral data of **4k** were taken from this mixture. – ^{1}H NMR ($CDCl_3$): δ = 1.03, 1.10 (2 s, 6H, 3-CH_3), 1.20 (t, J = 6.0 Hz, 3H, OCH_2CH_3), 1.77 (s, 3H, 2-CH_3), 3.10–4.06 (m, 5H, OCH_2CH_3, 4-, 5-H), 4.82 (br. s, 2H, C=CH_2).

1-(2-Bromo-1-ethoxypropyl)-2-methylenecyclohexane (**4l**): Compound **1c** (*E,Z* mixture, 1.57 g, 18.2 mmol), bromine (2.64 g, 16.5 mmol), $ZnCl_2$–Et_2O (3.6 ml, 6.90 mmol), and **3d** (3.10 g, 18.4 mmol) gave 4.70 g (99%) of **4l**. – ^{1}H NMR ($CDCl_3$): δ = 1.08–2.73 (m, 14H, 2 CH_3 and cyclohexane H), 3.33–4.56 (m, 5H, OCH_2CH_3, BrCH, OCH, CH), 4.60–4.93 (m, 2H, C=CH_2). On the basis of ^{1}H-NMR spectral data it could not be decided whether this was a mixture of two diastereoisomers or a single isomer.

2-Bromo-1-(2-cyclopenten-1-yl)-1-methoxy-1-phenylethane (**4m**) was obtained in 92% yield (2.83 g) from a 83:17 mixture of **1d** and acetophenone dimethyl acetal (1.47 g, total 11.0 mmol), bromine (1.60 g, 10.0 mmol), $ZnCl_2$–Et_2O (2.5 ml, 4.80 mmol), and **3e** (1.54 g, 11.0 mmol). – ^{1}H NMR (CCl_4): δ = 1.66–1.93 (m, 4H, CH_2CH_2), 3.29 (s, 3H, OCH_3), 3.38–4.06 (m, 3H, CH–CH=, $BrCH_2$), 5.68 (m_c, 2H, vinyl H), 7.21 (m_c, 5H, Ph).

2-Bromo-1-(2-cyclopenten-1-yl)-2-ethoxycyclohexane (**4n**): Enol ether **1e** (2.77 g, 22.0 mmol), bromine (3.20 g, 20.0 mmol), $ZnCl_2$–Et_2O (5.0 ml, 9.60 mmol), and **3e** (3.08 g, 22.0 mmol) gave 5.29 g (88%) of **4n**. – ^{1}H NMR ($CDCl_3$): δ = 0.99–2.57 (m, 15H, 6 CH_2, OCH_2CH_3), 3.28–4.04 (m, 3H, OCH_2CH_3, CH–CH=), 4.18 (m_c, 1H, BrCH), 5.78 (m_c, 2H, vinyl H).

2-Bromo-1-(2-cyclopenten-1-yl)-1-ethoxy-2-methylpropane (**4o**) was synthesized in 88% yield (1.20 g) from enol ether **1f** (550 mg, 5.49 mmol), bromine (800 mg, 5.00 mmol), $ZnCl_2$–Et_2O (1.3 ml, 2.52 mmol), and **3e** (770 mg, 5.50 mmol). – ^{1}H NMR ($CDCl_3$): δ = 0.95–1.32 (m, 4H, 5′-H_A, OCH_2CH_3), 1.52–2.50 [m, 9H, 4′-H, 5′-H_B, $C(CH_3)_2$], 3.11–3.75 (m, 4H, 1′-H, $CHOCH_2CH_3$), 5.69 (m_c, 2H, vinyl H).

Synthesis of the 1,4-Dienes

Elimination with Zinc/Ethanol (Procedure A): Crude **4h**, obtained from 11.0 mmol of **1d** and **3b**, was dissolved in absolute ethanol (28 ml). After addition of zinc powder (6.50 g, 100 mmol), the mixture was heated at reflux for 15 h. Pentane (40 ml) was added, the solvent mixture was decanted, and the remaining zinc powder was washed with four 20-ml portions of pentane. The combined solvents were successively washed with 10% aqueous NH_4Cl solution (40 ml) and with four 20-ml portions of water. The solvent was evaporated, and the residue was distilled to give 1.30 g (75%) of **5h** with b.p. 100°C (bath)/10–20 mbar (ref.[15] 90–92°C/16 mbar). For spectral data see below.

Elimination with Sodium in Diethyl Ether (Procedure B): Dry diethyl ether (40–50 ml) and sodium wire (3.79 g, 165 mmol) were placed into a 250-ml two-necked flask under nitrogen. Crude **4i**, prepared from 22.0 mmol of **1e** and **3b**, was added, and the mixture was heated under reflux for 4 h. The solvent was decanted, and the solid residue was washed with pentane (20 ml, 10 ml, and 5 ml). The solutions were combined, washed with two 40-ml portions of water (caution: small pieces of Na may be in the solution!), and dried with Na_2SO_4. After careful evaporation of the solvents, the residue was distilled to give 2.20 g (73%) of **5i** with b.p. 68°C (bath)/5–20 mbar. For spectral data see below.

2-Phenyl-1,4-pentadiene (**5d**): Compound **4d**, obtained from 22.0 mmol **1d** and **3a**, gave 2.50 g (79%) of **5d** according to procedure A. B.p. 80°C (bath)/22–30 mbar (ref.[15] 82–84°C/16 mbar). – ^{1}H NMR ($CDCl_3$): δ = 3.22 (br. d, J = 6.7 Hz, 2H, 3-H), 4.93–5.21 (m, 3H, 1-H_A, 5-H), 5.38 (s, 1H, 1-H_B), 5.88 (m_c, 1H, 4-H), 7.21–7.45 (m, 5H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 39.49 (t, C-3), 113.10 (t, C-1), 116.45 (t, C-5), 125.95 (d, C_o), 127.41 (d, C_p), 128.22 (d, C_m), 136.14 (d, C-4), 140.88 (s, C_i), 146.25 (s, C-2). – MS (70 eV): m/z (%) = 144 (100) [M^+], 129 (73) [$M^+ - CH_3$], 115 (10) [$M^+ - C_2H_5$], 103 (57) [$M^+ - C_3H_5$], 77 (16) [Ph^+].

$C_{11}H_{12}$ Calcd. 144.0939 Found 144.0932 (MS)

1-Allyl-1-cyclohexene (**5e**): Procedure A was used to prepare 272 mg (40% with respect to **1e**) from crude **4e**. B.p. 55°C (bath)/5–20 mbar (ref.[16] 154–158°C). – ^{1}H NMR ($CDCl_3$): δ = 1.54–1.64 (m, 4H, 4-, 5-H), 1.89–2.01 (m, 4H, 3-, 6-H), 2.67 (d, J = 6.9 Hz, 2H, allyl CH_2), 4.97–5.08 (m, 2H, CH=CH_2), 5.44 (m_c, 1H, 2-H), 5.70–5.91 (m, 1H, CH=CH_2). – ^{13}C NMR ($CDCl_3$): δ = 22.50, 22.97, 25.31, 28.34 (4 t, C-3, -4, -5, -6), 42.57 (t, CH_2CH), 115.44 (t, CH=CH_2), 121.87 (d, C-2), 136.30 (s, C-1), 136.97 (d, CH=CH_2). – MS (70 eV): m/z (%) = 122 (28) [M^+], 107 (14) [$M^+ - CH_3$], 93 (16) [$M^+ - C_2H_5$], 81 (100) [$M^+ - C_3H_5$].

C_9H_{14} Calcd. 122.1096 Found 122.1091 (MS)

2-Methyl-4-phenyl-1,4-pentadiene (**5h**) was synthesized according to procedure A (yield 75%, details see above) and procedure B (yield 2.26 g = 65% with respect to **1d**). – ^{1}H NMR ($CDCl_3$): δ = 1.72 (s, 3H, CH_3), 3.21 (s, 2H, 3-H), 4.77, 4.81 (2 m_c, 2H, 1-H), 5.11 (d, J = 1.4 Hz, 5-H), 5.43 (d, J = 1.5 Hz, 1H, 5-H), 7.27–7.46 (m, 5H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 22.28 (q, CH_3), 44.00 (t, C-3), 112.58, 114.27 (2 t, C-1, -5), 126.07 (d, C_o), 127.34 (d, C_p), 128.15 (d, C_m), 140.96, 143.39, 145.59 (3 s, C_i, C-2, -4). – MS (70 eV): *m/z* (%) = 158 (14) [M^+], 143 (100) [$M^+ - CH_3$], 128 (30) [$M^+ - 2\,CH_3$], 103 (33) [$M^+ - C_4H_7$], 77 (22) [Ph^+].

$C_{12}H_{14}$ Calcd. 158.1096 Found 158.1095 (MS)

1-(2-Methylallyl)-1-cyclohexene (**5i**) was prepared following procedure A (yield 459 mg = 61% with respect to **1e**) and B (yield 74%, details see above). – ^{1}H NMR ($CDCl_3$): δ = 1.50–1.64 (m, 7H, CH_3, 4-, 5-H), 1.81–2.10 (m, 4H, 3-, 6-H), 2.63 (s, 2H, allyl CH_2), 4.70, 4.75 (2 m_c, 2H, C=CH_2), 5.46 (m_c, 1H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 21.84 (q, CH_3), 22.49, 23.00, 25.35, 27.70 (4 t, C-3, -4, -5, -6), 47.14 (t, CH_2), 111.28 (t, C=CH_2), 123.00 (d, C-2), 135.51 (s, C-1), 144.28 (s, C=CH_2). – MS (70 eV): *m/z* (%) = 136 (30) [M^+], 121 (64) [$M^+ - CH_3$], 107 (21) [$M^+ - C_2H_5$], 93 (49) [$M^+ - C_3H_7$], 81 (100) [$M^+ - C_4H_7$].

$C_{10}H_{16}$ Calcd. 136.1252 Found 136.1257 (MS)

2,5-Dimethyl-1,4-hexadiene (**5j**) has been synthesized according to procedure A (yield 122 mg = 20% with respect to **1f**) and procedure B (1.52 g = 72% with respect to **1f**). B.p. 89°C (bath)/150–190 mbar (ref.[17]) does not report the b.p.). – ^{1}H NMR ($CDCl_3$): δ = 1.63, 1.72 [2 br. s, 9H, 2-CH_3, $C(CH_3)_2$], 2.68 (br. d, J = 7.1 Hz, 2H, 3-H), 4.69 (m_c, 2H, 1-H), 5.19 (m_c, 1H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 17.62, 22.55, 25.77 (3 q, 3 CH_3), 36.59 (t, C-3), 109.71 (t, C-1), 121.94 (d, C-4), 132.92 (s, C-5), 145.46 (s, C-2). – MS (70 eV): *m/z* (%) = 110 (52) [M^+], 95 (100) [$M^+ - CH_3$], 67 (47) [$M^+ - C_3H_7$].

C_8H_{14} Calcd. 110.1096 Found 110.1098 (MS)

2,3,3-Trimethyl-1,4-pentadiene (**5k**): The mixture of **4k** and hexaethyldisiloxane described above was treated with Na (procedure B) to give 1.50 g (62% with respect to **1a**) of **5k**. B.p.[18] 102°C. – ^{1}H NMR ($CDCl_3$): δ = 1.15 [s, 6H, $C(CH_3)_2$], 1.70 (m_c, 3H, 2-CH_3), 4.74–4.82 (m, 2H, 5-H), 4.93–5.03 (m, 2H, 1-H), 5.82 (m_c, 1H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 19.74 (q, 2-CH_3), 26.01 [q, $C(CH_3)_2$], 42.18 (s, C-3), 109.30, 110.87 (2 t, C-1, -5), 147.14 (d, C-4), 151.61 (s, C-2). – MS (70 eV): *m/z* (%) = 110 (20) [M^+], 95 (100) [$M^+ - CH_3$], 67 (44) [$M^+ - C_3H_7$], 41 (47) [$C_3H_5^+$].

C_8H_{14} Calcd. 110.1096 Found 110.1098 (MS)

1-Methylene-2-((E,Z)-1-propenyl)cyclohexane (**5l**): Treatment of crude **4l** (4.70 g) with Na according to procedure B gave 1.60 g (64% with respect to **1c**) of **5l** as a mixture of (*E*)- and (*Z*)-**5l**. B.p. 90°C (bath)/16–90 mbar. – ^{1}H NMR ($CDCl_3$): δ = 1.20–1.90 (m, 9H, 3-, 4-, 5-H, CH_3), 2.02–2.22, 2.32–2.50 (2 m, 2H, 6-H), 2.66–2.80, 2.98–3.12 (2 m, 1H, 2-H), 4.64–4.80 (m, 2H, C=CH_2), 5.40–5.72 (m, 2H, CH=CH). – ^{13}C NMR ($CDCl_3$): δ = 12.96 (q, CH_3, *Z*), 18.08 (q, CH_3, *E*), 25.07, 25.42, 28.16, 28.27, 34.45, 34.79, 35.29, 35.54 (8 t, C-3, -4, -5, -6, *E,Z*), 41.14, 46.59 (2 d, C-2, *E,Z*), 106.10, 106.34 (2 t, C=CH_2, *E,Z*), 123.95, 124.86 (2 d, CH_3CH=CH, *E,Z*), 132.77, 133.69 (2 d, CH_3CH=CH, *E,Z*), 151.00, 152.54 (2 s, C-1, *E,Z*). – MS (70 eV): *m/z* (%) = 136 (64) [M^+], 121 (60) [$M^+ - CH_3$], 107 (50) [$M^+ - C_2H_5$], 93 (76) [$M^+ - C_3H_7$], 79 (100) [$M^+ - C_2H_5 - C_2H_4$].

$C_{10}H_{16}$ Calcd. 136.1252 Found 136.1256 (MS)

3-(1-Phenylvinyl)-1-cyclopentene (**5m**): 1.41 g of compound **5m** was obtained from crude **4m** and Zn (procedure A). Yield: 75% (with respect to **1d**). B.p. 87–110°C (bath)/2–4 mbar. – ^{1}H NMR ($CDCl_3$): δ = 1.46–1.68 (m, 1H, 4-H_A), 2.10–2.48 (m, 3H, 4-H_B, 5-H), 3.85 (m_c, 1H, 3-H), 5.03, 5.25 (2 m_c, 2H, C=CH_2), 5.70–5.92 (m, 2H, 1-, 2-H), 7.25–7.47 (m, 5H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 31.14, 32.00 (2 t, C-4, -5), 49.77 (d, C-3), 110.81 (t, C=CH_2), 126.38 (d, C_o), 127.19 (d, C_p), 128.17 (d, C_m), 131.90, 133.29 (2 d, C-1, -2), 141.95 (s, C_i), 152.24 (s, C=CH_2). – MS (70 eV): *m/z* (%) = 170 (100) [M^+], 155 (57) [$M^+ - CH_3$], 103 (75) [M^+ – cyclopentenyl], 77 (52) [Ph^+], 67 (40) [cyclopentenyl$^+$].

$C_{13}H_{14}$ Calcd. 170.1096 Found 170.1086 (MS)

1-(2-Cyclopenten-1-yl)-1-cyclohexene (**5n**): Procedure B yielded 1.77 g (54% with respect to **1e**) of **5n** from crude **4n**. B.p. 100°C/16–20 mbar (ref.[19]) does not report the b.p.). – ^{1}H NMR ($CDCl_3$): δ = 1.50–1.78 (m, 5H), 1.89–2.22 (m, 5H), 2.37 (m_c, 2H), 3.27 (m_c, 1H, 3-H), 5.43 (m_c, 1H), 5.64–5.90 (m, 2H, 1-, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 22.73 (t), 23.09 (t), 25.24 (t), 26.40 (t), 29.30 (t), 32.38 (t), 52.93 (d), 119.73 (d), 131.23 (d), 133.65 (d), 140.97 (s). – MS (70 eV): *m/z* (%) = 148 (86) [M^+], 133 (15) [$M^+ - CH_3$], 119 (36) [$M^+ - C_2H_5$], 105 (33) [$M^+ - C_3H_7$], 91 (65) [$M^+ - C_4H_9$], 80 (100), 77 (25), 67 (53) [cyclopentenyl$^+$].

$C_{11}H_{16}$ Calcd. 148.1252 Found 148.1258 (MS)

3-(2-Methyl-1-propenyl)-1-cyclopentene (**5o**) was prepared according to procedure A (yield 200 mg = 30% with respect to **1f**) and procedure B (1.80 g = 67% with respect to **1f**). B.p. 73°C (bath)/30–45 mbar (ref.[19]) does not report the b.p.). – ^{1}H NMR ($CDCl_3$): δ = 1.36–1.55 (m, 1H, 4-H_A), 1.67, 1.69 [2 br. s, 6H, $C(CH_3)_2$], 2.02–2.40 (m, 3H, 4-H_B, 5-H), 3.49 (m_c, 1H, 3-H), 5.00 (br. d, J = 9.1 Hz, 1H, C=CH), 5.50–5.80 (m, 2H, 1-, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 17.93, 25.73 [2 q, $C(CH_3)_2$], 31.19, 32.22 (2 t, C-4, -5), 44.25 (d, C-3), 129.13, 130.45 (2 d, C-1, -2), 130.60 [s, $(CH_3)_2C$=CH], 134.72 [d, (CH_3)C=CH]. – MS (70 eV): *m/z* (%) = 122 (50) [M^+], 107 (100) [$M^+ - CH_3$], 79 (64) [$M^+ - C_3H_7$], 67 (17) [cyclopentenyl$^+$].

C_9H_{14} Calcd. 122.1096 Found 122.1098 (MS)

The reaction with Zn in ethanol gave compounds **6** and **7** in addition to **5o**. These two ethers (**6**, **7**) were adsorbed, when the product mixture was passed through silica with pentane as eluent, and eluted with CH_2Cl_2. The 2:1 mixture of **6** and **7** was identified by ^{13}C-NMR spectroscopy. – *3-(2-Cyclopenten-1-yl)-3-ethoxy-2-methyl-1-propene* (**6**): ^{13}C NMR ($CDCl_3$): δ = 15.29 (q, OCH_2CH_3), 16.76 (q, CH_3), 27.30, 31.96 (2 t, C-3, -4), 48.59 (d, C-3), 63.37 (t, OCH_2CH_3), 88.18 (d, CH), 114.11 (t, C=CH_2), 131.51, 132.08 (2 d, CH=CH), 144.45 (s, C=CH_2). – *1-(2-Cyclopenten-1-yl)-1-ethoxy-2-methylpropane* (**7**): ^{13}C NMR ($CDCl_3$): δ = 15.83 (q, OCH_2CH_3), 18.11, 20.21 [2 q, $CH(CH_3)_2$], 25.15, 32.10 (2 t, C-4, -5), 31.87 [d, $CH(CH_3)_2$], 48.90 (d, C-3), 68.27 (t, OCH_2CH_3), 87.84 (d, CH), 131.62, 132.87 (2 d, C-1, -2).

CAS Registry Numbers

1a: 109-92-2 / **1b**: 116-11-0 / **1c** (*E*): 4696-26-8 / **1c** (*Z*): 4696-25-7 / **1d**: 4747-13-1 / **1e**: 1122-84-5 / **1f**: 927-61-7 / **3a**: 762-72-1 / **3b**: 18292-38-1 / **3c**: 64545-12-6 / **3d**: 58541-14-3 / **3e**: 14579-08-9 / **4a**: 22089-55-0 / **4b**: 135312-62-8 / **4c** (*R*,R**): 135312-63-9 / **4c** (*R*,S**): 135312-79-7 / **4d**: 135312-64-0 / **4e**: 135312-65-1 / **4f**: 135312-66-2 / **4g**: 135312-67-3 / **4h**: 135312-68-4 / **4i**: 135312-69-5 / **4j**: 135312-70-8 / **4k**: 135312-71-9 / **4l**: 135312-72-0 / **4m**: 135312-73-1 / **4n**: 135312-74-2 / **4o**: 135312-75-3 / **5a**: 591-93-5 / **5b**: 763-30-4 / **5c** (*E*): 7319-00-8 / **5c** (*Z*): 7318-67-4 / **5d**: 35342-69-9 / **5e**: 13511-13-2 / **5f**: 763-88-2 / **5g**: 4161-65-3 / **5h**: 52713-62-9 / **5i**: 135312-76-4 / **5j**: 927-97-9 / **5k**: 756-02-5 / **5l** (*E*): 135312-77-5 / **5l** (*Z*): 135312-80-0 / **5m**: 135312-78-6 / **5n**: 119946-62-2 / **5o**: 16839-59-1

* Dedicated to Professor *Karl Heinz Büchel* on the occasion of his 60th birthday.

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[220/91]