Pergamon

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Tetrahedron Letters 44 (2003) 7541–7544

TETRAHEDRON LETTERS

Formation of (*E*) 1-alkoxy-1,3-butadienes from corresponding propargyl ethers; vicarious nucleophilic substitution in alkoxyallenes

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Received 13 June 2003; revised 23 July 2003; accepted 31 July 2003

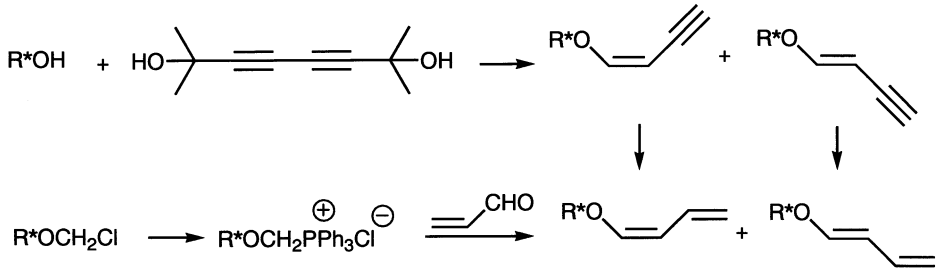
Abstract—Propargyl ethers treated with dimsyl anion in DMSO at 80–100°C undergo terminal methylenation to afford corresponding (*E*) 1-alkoxy-1,3-butadienes. The reaction proceeds via an alkoxy-allene.

1-Alkoxy-1,3-butadienes represent an important class of reactive compounds particularly useful in a variety of Diels–Alder reactions.[1] Simple methoxy- or ethoxy-butadienes have been obtained as a mixture of (*E*) and (*Z*) isomers via acid promoted degradation of the corresponding 1,1,3-trialkoxybutanes.[2] Chiral alkoxy-butadienes are obtained via a two-step transformation which consists of formation of (*E*) and (*Z*) ene-yne mixture, separation of isomers, and hydrogenation of the triple bond (Scheme 1).[3] Alternatively, the same mixture of alkoxybutadienes can be obtained via the Wittig reaction (Scheme 1).[3]

We have found that readily available propargyl ethers[4] can be easily transformed into the corresponding (*E*) 1-alkoxy-1,3-butadienes via reaction with dimsyl sodium. To demonstrate the usefulness of this new reaction we selected three simple propargyl ethers **1**–**3** and three chiral propargyl ethers derived from sugars **4**–**6**. The reaction proceeds with dimsyl anion[5] dissolved in DMSO at 80–100°C.[6]

Transformation of the methyl propargyl ether **1** failed to afford 1-methoxybutadiene **9**. The yields of *t*-butoxy-[7] and *n*-butoxy-butadienes **10** and **11** derived from the corresponding propargyl ethers **2**[8] and **3**[9] did not exceed 18%. The dienes **12**–**14** were formed in about 50% yield.[6] The lower yields of simple dienes can be explained by their assumed tendency to polymerization under the reaction conditions. In no case did we observe the formation of (*Z*) isomers of butadienes **10**–**14**.[6]

It is well known that at lower temperatures (up to 40°C) under the same conditions the propargyl ethers undergo isomerisation to the corresponding alkoxy-allenes.[10,11] The formation of 1,3-butadienes from propargyl ethers is preceded by their initial isomeriza-



Scheme 1.

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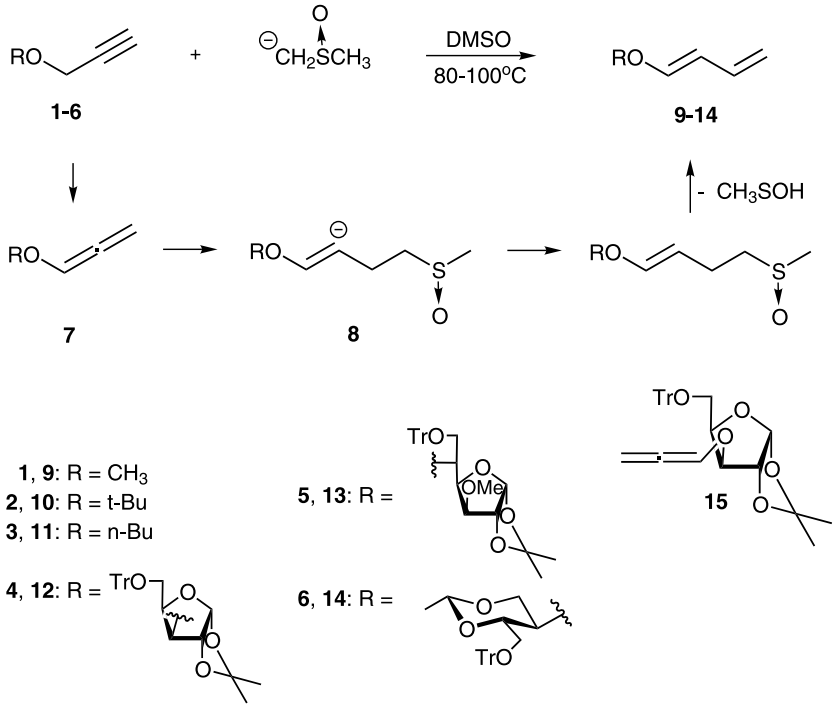
doi:10.1016/S0040-4039(03)01867-7

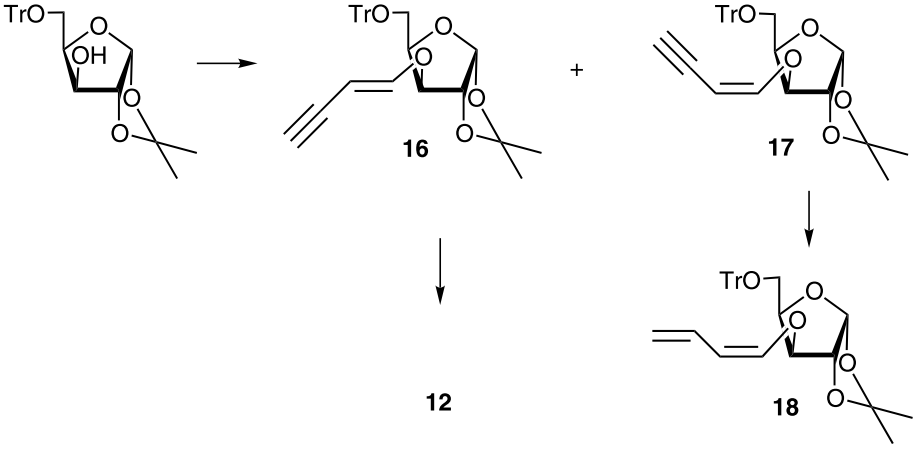
tion to the corresponding cumulenes; this was exemplified by the transformation of the known alkoxyallene **15**[10] into butadiene **12** under the same conditions as transformation of **4** into **12**. It can be assumed that the addition of dimsyl anion to the allene **7** is followed by protonation of unstable carbanion **8** by DMSO and subsequent elimination of sodium methylsulfinate (Scheme 2). The observed high (*E*)-stereoselectivity of the vinyl ether fragment is created at the addition step of dimsyl anion to the cumulene. It can be assumed that the repulsion between the alkoxyl and methylene groups at the stage of formation of **8** helps to decide on the configuration of the vinyl ether double bond. For structural comparison, the (*E*) and (*Z*) dienes **12** and **18**[6] were obtained from the corresponding (*E*) and (*Z*) ene-ynes **16** and **17**,[12] respectively, using the standard methodology shown in Scheme 1 (Scheme 3). Examination of the $J_{1'2'}$ coupling constants unequivocally proves the (*E*) and (*Z*) configuration of the resulting dienes.[6]

The methylenation of propargyl ethers (alkoxy-allenes) with dimsyl sodium is a new reaction. Its mechanism (Scheme 2) resembles that of vicarious nucleophilic substitution of hydrogen (VNS).[13] The similar methylation reaction by dimsyl anion in DMSO that can be considered as a VNS type reaction has also been reported for nitroarenes and certain heterocycles.[14]

Although the yield of transformations of propargyl ethers into corresponding alkoxy-butadienes is rather moderate, the simplicity of the procedure and configurational purity of the corresponding dienes formed should be emphasized. The synthesis should be particu-



Scheme 2.



Scheme 3.

larly useful for the preparation of complex 1-alkoxy-1,3-butadienes, more resistant to polymerization.

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6. **Representative experimental procedure**:
   To a solution of methylsulfinyl carbanion in DMSO[5] (3 mL) at 80–100°C, compound **4** (0.2 g, 0.42 mmol) was added. The resulting dark solution was stirred for 3 h at the same temperature. Subsequently, the mixture was cooled, poured into cold water (20 mL) and extracted with *t*-butyl methyl ether (3×10 mL). The combined extracts were purified by the chromatography to give pure **12** (0.095 g, 46%); mp 124.5–125.5°C; $[\alpha]_D=-2.9$ (*c* 0.4, CH_2Cl_2); IR ($CHCl_3$): 1640, 1654 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 6.41 (d, 1H, $J=12.5$ Hz, H-1′), 6.15 (dt, 1H, $J=16.8$, 10.7 Hz, H-3′), 5.85 (d, 1H, $J=3.8$ Hz, H-1), 5.62 (dd, 1H, $J=10.7$, 12.5 Hz, H-2′), 5.03 (dd, 1H, $J=1.7$, 16.8 Hz, H-4′a), 4.86 (dd, 1H, $J=1.7$, 10.7 Hz, H-4′b), 4.54 (d, 1H, $J=3.8$ Hz, H-2), 4.35–4.44 (m, 2H, H-3, H-4), 3.45 (dd, 1H, $J=5.1$, 9.2 Hz, H-5a), 3.29 (dd, 1H, $J=7.2$, 9.2 Hz, H-5b), 1.52, 1.32 (2s, 6H, isopropyl); HRMS (LSIMS) *m/z* calcd for $C_{31}H_{32}O_5Na$ $(M+Na)^+$ 507.2147, found 507.2147. Anal. calcd for $C_{31}H_{32}O_5$: C, 76.84; H, 6.65. Found: C, 76.74; H, 6.75.
   Compound **18** was obtained from **17**[12] following the known procedure:[3] oil; $[\alpha]_D=-25.9$ (*c* 0.9, CH_2Cl_2); IR ($CHCl_3$): 1648 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.43 (ddt, 1H, $J=0.9$, 17.2, 10.5 Hz, H-3′), 6.00 (bd, 1H, $J=6.1$ Hz, H-1′), 5.84 (d, 1H, $J=3.7$ Hz, H-1), 5.10 (dd, 1H, $J=6.1$, 10.5 Hz, H-2′), 5.05 (dm, 1H, $J=17.2$ Hz, H-4′a), 4.87 (dm, 1H, $J=10.5$ Hz, H-4′b), 4.55 (d, 1H, $J=3.7$ Hz, H-2), 4.37 (ddd, 1H, $J=2.9$, 5.5, 7.8 Hz, H-4), 4.31 (d, 1H, $J=2.9$ Hz, H-3), 3.45 (dd, 1H, $J=5.5$, 9.1 Hz, H-5a), 3.37 (dd, 1H, $J=7.8$, 9.1 Hz, H-5b), 1.52, 1.31 (2s, 6H, isopropyl); HRMS (LSIMS) *m/z* calcd for $C_{31}H_{32}O_5Na$ $(M+Na)^+$ 507.2147, found 507.2169. Anal. calcd for $C_{31}H_{32}O_5$: C, 76.84; H, 6.65. Found: C, 76.94; H, 6.69.
   Analytical and spectral data of compounds 5, 6, 11, 13, 14:
   5: mp 104–106°C; $[\alpha]_D=-44.3$ (*c* 1.3, CH_2Cl_2); IR (film): 3288, 2115 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 5.82 (d, 1H, $J=3.8$ Hz, H-1), 4.60 (d, 1H, $J=3.8$ Hz, H-2), 4.38 (dd, 1H, $J=2.4$, 15.4 Hz, H-1′a), 4.26 (dd, 1H, $J=3.0$, 9.4 Hz, H-4), 4.20 (dd, 1H, $J=2.4$, 15.4 Hz, H-1′b), 3.96 (ddd, 1H, $J=2.0$, 5.9, 9.4 Hz, H-5), 3.83 (d, 1H, $J=3.0$ Hz, H-3), 3.48 (dd, 1H, $J=2.0$, 10.4 Hz, H-6a), 3.44 (s, 3H, OCH_3), 3.27 (dd, 1H, $J=5.9$, 10.4 Hz, H-6b), 2.38 (t, 1H, $J=2.4$ Hz, H-3′), 1.30, 1.46 (2s, 6H, isopropyl); HRMS (LSIMS) *m/z* calcd for $C_{32}H_{34}O_6Na$ $(M+Na)^+$ 537.2253, found 537.2266. Anal. calcd for $C_{32}H_{34}O_6$: C, 74.71; H, 6.67. Found: C, 75.02; H, 6.90.
   6: mp 65–67°C; $[\alpha]_D=-37.5$ (*c* 0.3, CH_2Cl_2); IR (CH_2Cl_2): 3303, 2120 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 4.70 (q, 1H, $J=5.0$ Hz, H-2), 4.30 (dd, 1H, $J=5.3$, 10.8 Hz, H-6a), 3.97 (d, 2H, H-1″a, 1″b), 3.84 (ddd, 1H, $J=5.3$, 9.5, 10.8 Hz, H-5), 3.52 (ddd, 1H, $J=2.0$, 4.0, 9.5 Hz, H-4), 3.41 (dd, 1H, $J=2.0$, 10.3 Hz, H-1′a), 3.39 (t, 1H, $J=10.8$ Hz, H-6b), 3.14 (dd, 1H, $J=4.0$, 10.3 Hz, H-1′b), 2.31 (t, 1H, $J=2.4$ Hz, H-3″), 1.42 (d, 3H, $J=5.0$ Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 144.0, 128.8, 127.7, 126.9, 98.8, 86.3, 79.6, 79.5, 74.5, 68.9, 68.6, 63.0, 57.8, 20.6 HRMS (LSIMS) *m/z* calcd for $C_{28}H_{28}O_4Na$ $(M+Na)^+$ 451.1885, found 451.1874. Anal. calcd for $C_{28}H_{28}O_4$: C, 78.48; H, 6.59. Found: C, 78.59; H, 6.62.
   11: bp (air bath) 60°C; IR (film): 1642 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.48 (d, 1H, $J=12.5$ Hz, H-1), 6.14 (dt, 1H, $J=10.7$, 16.9 Hz, H-3), 5.49 (dd, 1H, $J=10.7$, 12.5 Hz, H-2), 4.41 (m, 1H, H-4a), 4.72 (m, 1H, H-4b), 3.67 (t, 2H, $-CH_2O$), 1.57, 1.34, 0.87 (3×m, 7H, C_3H_7); ^{13}C NMR ($CDCl_3$): δ 151.1, 133.6, 111.2, 106.9, 69.6, 31.2, 19.1, 13.8. HRMS (EI) *m/z* calcd for $C_8H_{14}O$ M^+ 126.1045, found 126.1046.
   13: oil; $[\alpha]_D=-5.5$ (*c* 1.2, CH_2Cl_2); IR (film): 1653 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.59 (d, 1H, $J=12.1$ Hz, H-1′), 6.22 (dt, 1H, $J=11.0$, 11.0, 16.7 Hz, H-3′), 5.79 (d, 1H, $J=3.8$ Hz, H-1), 5.72 (dd, 1H, $J=11.0$, 12.1 Hz, H-2′), 4.99 (dd, 1H, $J=1.8$, 16.7 Hz, H-4′a), 4.82 (dd, 1H, $J=1.8$, 11.0 Hz, H-4′b), 4.51 (d, 1H, $J=3.8$ Hz, H-2), 4.23 (dd, 1H, $J=3.0$, 9.4 Hz, H-4), 4.15 (ddd, 1H, $J=2.0$, 6.7, 9.4 Hz, H-5), 3.74 (d, 1H, $J=3.0$ Hz, H-3), 3.42 (dd, 1H, $J=2.0$, 10.3 Hz, H-6a), 3.36 (s, 3H, OCH_3), 3.30 (dd, 1H, $J=6.7$, 10.3 Hz, H-6b), 1.21, 1.45 (2×s, 6H, isopropyl); ^{13}C NMR ($CDCl_3$): δ 151.5, 143.9, 133.3, 128.8, 127.7, 126.9, 111.7, 111.5, 109.0, 105.2, 86.7, 83.3, 81.3, 78.3, 78.2, 64.3, 57.7, 26.7, 26.3. Anal. calcd for $C_{33}H_{36}O_6$: C, 74.98; H, 6.86. Found: C, 74.28; H, 7.01.
   14: oil; $[\alpha]_D=-11.4$ (*c* 1.0, CH_2Cl_2); IR (film): 1654, 1643 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 6.35 (d, 1H, $J=12.2$ Hz, H-1″), 6.05 (dt, 1H, $J=10.6$, 10.8, 16.9 Hz, H-3″), 5.55 (dd, 1H, $J=10.8$, 12.2 Hz, H-2″), 4.92 (dd, 1H, $J=1.2$, 16.9 Hz, H-4″a), 4.82 (dd, 1H, $J=1.2$, 10.6 Hz, H-4″b), 4.74 (q, 1H, $J=5.0$ Hz, H-2), 4.26 (dd, 1H, $J=5.3$, 10.6 Hz, H-6a), 4.15 (m, 1H, H-5), 3.60 (ddd, 1H, $J=2.0$, 3.8, 9.3 Hz, H-4), 3.46 (t, 1H, $J=10.6$ Hz, H-6b), 3.41 (dd, 1H, $J=1.9$, 10.5 Hz, H-1′a), 3.14 (dd, 1H, $J=3.8$, 10.5 Hz, H-1′b), 1.43 (d, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 149.7, 144.0, 132.7, 128.8, 127.7, 126.9, 112.3, 109.5, 99.1, 86.4, 79.1, 69.9, 68.4, 62.5, 20.5; HRMS (ESI) *m/z* calcd for $C_{29}H_{30}O_4Na$ $(M+Na)^+$ 465.2036, found 465.2039. Anal. calcd for $C_{29}H_{30}O_4$: C, 78.71; H, 6.83. Found: C, 77.62; H, 7.18.

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