Synthesis and Reactivity of Allenylvinyl Cycloalk-2-enyl Ethers

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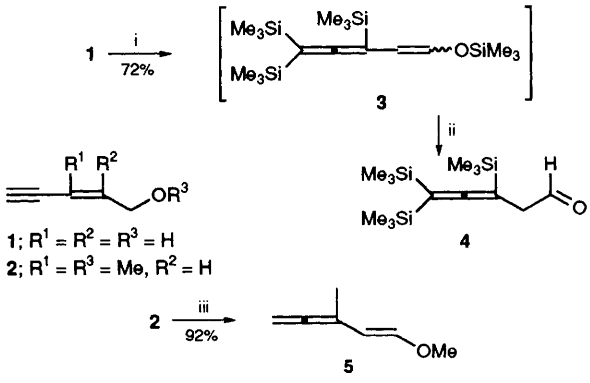
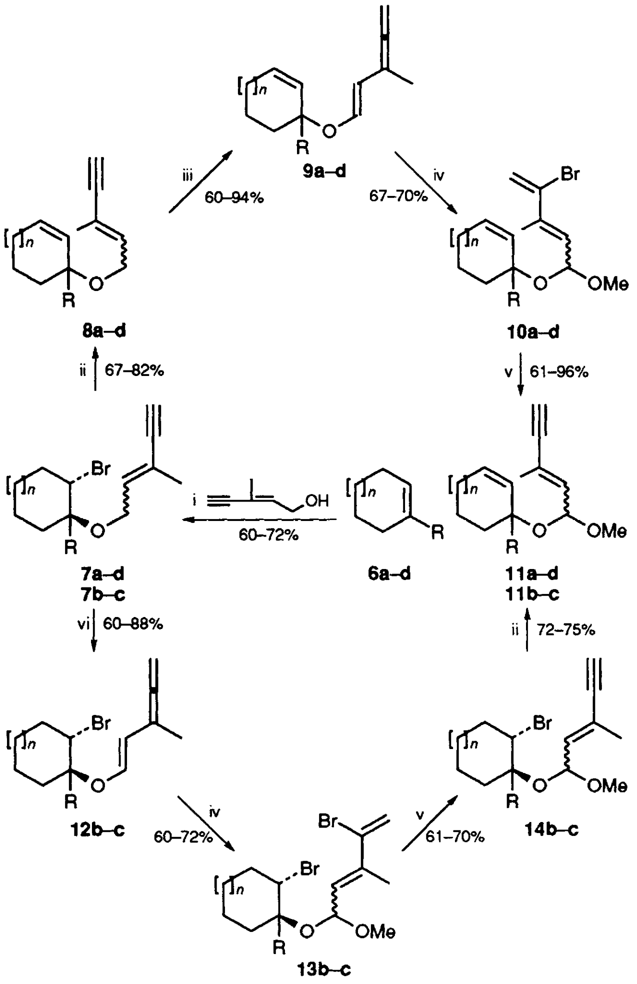
Cohalogenation of alkenes **6** by *N*-bromosuccinimide (NBS) in 3-methylpent-2-en-4-yn-1-ol provides β-bromo-3-methylpent-2-en-4-ynyl ether **7** precursors of 3-(penta-1,3,4-trienyloxy)cycloalkenes **9** which react chemo- and regio-selectively with NBS in methanol to give bromovinyl acetals **10**.

In connection with our continuing studies on the reactivity and synthetic application of allenyl ethers,[1] we required to prepare compounds incorporating the structure of penta-1,3,4-trienyl ethers of type **5** (Scheme 1). Although extensive work on the synthesis of the corresponding isomeric penta-1,2,4-trienyl ethers has been reported,[2] the preparation of compound **5** has received only a little attention. Allenyl silyl enol ethers[3] or trifluoromethylsulfonyl ethers[4] can be obtained by 1,6-addition of lithium dimethylcuprate to acceptor-substituted enynes followed by treatment with the appropriate electrophile. Other procedures involve the ring cleavage of 2-furfuryl carbanions[5] or the [2 + 2] cycloaddition of ynamines with silyl vinyl ketenes.[6] However, as yet, general methods for the synthesis of these derivatives are not available. In the course of mechanistic studies, we observed that β-allenic aldehydes **4** can easily be obtained by treatment of pent-2-en-4-yn-1-ol **1** with excess of BuLi (4 equiv.), quenching with $ClSiMe_3$ (4 equiv.) and then acidic work up. We showed that this transformation evolved *via* the allenyl silyl enol ether **3**, since treating 1-methoxy-3-methylpent-2-en-4-yne **2** with 0.5 equiv. of Bu^{t}OK in dimethyl sulfoxide (DMSO) provided 1-methoxy-3-methylpenta-1,3,4-triene **5**† in 92% yield. The easy base-catalysed isomerization of **2** prompted us to prepare and study the reactivity of β-bromo-pent-2-en-4-ynyl ethers **7** (Scheme 2). These compounds were obtained in 60–72% yields by halogenation of alkenes **6** by *N*-bromosuccinimide (NBS) in 3-methylpent-2-en-4-yn-1-ol at −30 °C.‡ Selective dehydrohalogenation of **7** in diazabicycloundecene (DBU) led to allyl pent-2-en-4-ynyl ethers **8**, which under isomerization conditions (Bu^{t}OK, 0.5 equiv.) gave allyl vinyl ethers **9** (60–94%). Interestingly, halogenation of **9** by NBS in methanol in the presence of K_2CO_3 (1 equiv.) proceeded chemo- and regio-selectively by 1,4-addition to afford the sensitive bromovinyl acetals **10**. These compounds were obtained in good yields, providing the HBr was neutralized as soon as it was generated. Furthermore, Bu^{t}OK promoted dehydrohalogenation of **10** resulted in the formation of allyl 2-en-4-ynyl mixed acetals **11**.§ The overall sequence isomerization–halogenation–dehydrohalogenation provides an efficient conversion of ethers **8** into the corresponding acetals **11**.

An alternative route to **11b–c** involves the base-catalysed isomerization of **7b–c** (Bu^{t}OK, 0.3 equiv.) into β-bromo



Scheme 1 *Reagents and conditions*: i, BuLi, $ClSiMe_3$ (4 equiv.); ii, 5% HCl; iii, Bu^{t}OK (0.5 equiv., DMSO, 15 °C, 0.5 h)



a; *n* = 0, R = H
b; *n* = 1, R = H
c; *n* = 1, R = Me
d; *n* = 2, R = H

Scheme 2 *Reagents and conditions*: i, NBS (−30 °C, 3 h); ii, DBU, (110 °C, 3 h); iii, Bu^{t}OK (0.5 equiv., benzene, 60 °C, 1 h); iv, NBS, MeOH, K_2CO_3 (1 equiv., −40 °C, 1 h); v, Bu^{t}OK (1.2 equiv., 20 °C, 12 h); vi, Bu^{t}OK (0.3 equiv., pentane, 25 °C, 12 h)

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† **5**: IR, ν/cm^{-1} 2940, 1945, 1635 and 1140; NMR (200 MHz, $CDCl_3$): ^{1}H, δ 6.40 (d, 1H *J* 12.9 Hz), 5.36 (d, 1H, *J* 12.9 Hz), 4.75 (q, d, 2H, *J* 2.9 Hz), 3.56 (s, 3H) and 1.75 (t, 3H, *J* 2.9 Hz); ^{13}C δ 209.6, 146.7, 102.5, 96.6, 74.1, 55.6 and 15.4.

‡ Satisfactory analytical and spectral data were obtained for all compounds.

§ **10b** (mixture of isomers): IR ν/cm^{-1} 3300, 3040, 2940, 2100, 1645, 1130 and 1040; NMR (200 MHz, $CDCl_3$): ^{1}H δ 5.85 (d, 1H, *J* 6.4 Hz), 5.78 (m, 2H), 5.30, 5.21 (2d, 1H, *J* 6.4 Hz), 4.11 (m, 1H), 3.25, 3.24 (2s, 3H), 2.80 (s, 1H), 1.83 (s, 3H) and 1.92–1.18 (m, 6H); ^{13}C, 135.5, 135.4, 131.0, 130.8, 128.1, 127.5, 86.0, 76.0, 69.0, 51.7, 51.3, 29.9, 28.8, 24.93, 24.89, 19.1, 19.0 and 17.8.

allenyl vinyl ethers **12b–c**. 1,4-Halogenation of **12b–c** by NBS in methanol provided **13b–c**, precursors of β-bromo mixed acetals **14b–c** by selective dehydrohalogenation. Bis allyl mixed acetals **11b–c** were isolated subsequently upon treatment with DBU.

Our results show that the combination of the halogenation of alkenes and the base-catalysed isomerization of pent-2-en-4-ynyl ethers provide a novel, general and efficient access to a new class of polyunsaturated derivatives which can be used as building blocks in organic synthesis.[7]

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