Diels–Alder Intramolecular Cycloaddition of Vinylallenyl Cycloalken-3-yl Ethers

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Cohalogenation of cycloalkenes **1** by *N*-bromosuccinimide (NBS) in 4-methylpent-4-en-2-yn-1-ol affords β-bromopent-4-en-2-ynyl ethers **2** which undergo facile base-promoted consecutive dehydrohalogenation–isomerization–intramolecular Diels–Alder cycloaddition leading to tricyclic conjugated enol ethers **6**.

The ability of vinylallenes to participate as dienes in Diels–Alder type cycloadditions[1] constitutes a convenient route for the construction of complex ring systems.

Although intramolecular cycloadditions of allenyl ether dienophiles have been well studied,[2] reactions involving vinyl allenyl ether dienes have received little attention.[3] Our interest in the reactivity of allyl allenyl ethers[4] has prompted us to prepare and study the intramolecular cycloaddition of a series of allyl vinylallenyl ethers **5**.

It has been shown that allyl-4-methylpent-4-en-2-ynyl ethers do not undergo base-catalysed cycloadditions;[3] we report here the synthesis and the extra reactivity of the cyclic analogues **3**, which, under the same base-catalysed reaction conditions, lead to tricyclic conjugated enol ethers **6** by consecutive isomerization [4 + 2] Diels–Alder reaction.

Halogenation of cycloalkenes **1** by *N*-bromosuccinimide (NBS) in 4-methylpent-4-en-2-yn-1-ol afforded the β-bromopent-4-en-2-ynyl ethers **2** in 70–75% yield, the reaction being regio- and stereo-selective.† Treating **2** with 1.3 equiv. of Bu^{t}OK in refluxing benzene for 2 h resulted in the formation of **6**‡ in 80–85% yield; dehydrobromination of **2** in diazabicycloundecene (DBU, 3 equiv. 60 °C, 3 h) gave rise to allyl pent-4-en-2-ynyl ethers **3** (72–97%), which undergo catalytic isomerization (Bu^{t}OK, 0.3 equiv., in refluxing pentane) into enol ethers **6** (90–95%). On the other hand, treatment of **2a, b** under the same catalytic conditions resulted in the isomeriza-

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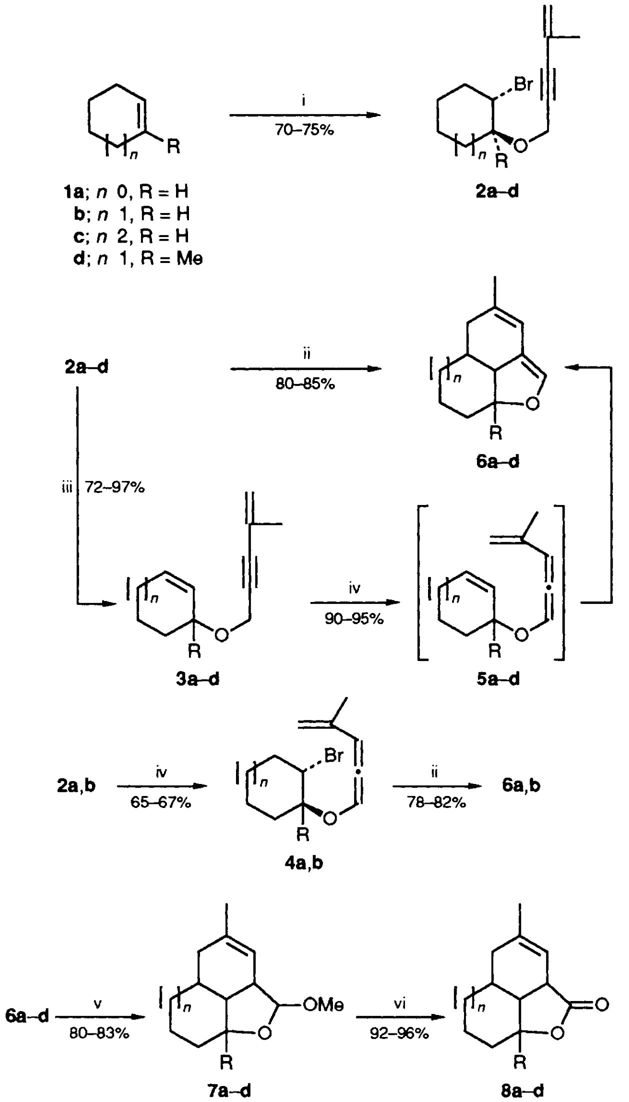
† Satisfactory analytical and spectral data were obtained for all compounds.

‡ **6b**: ^{1}H NMR (CDCl$_3$) (200 MHz) δ 6.16 (s, br, 1H); 5.90 (s, br, 1H); 4.46 (q, *J* 7.0 Hz, 1H); 2.96 (t, br, *J* 7.0 Hz, 1H); 2.15 (m, 1H); 1.8–1.7 (m, 2H); 1.65 (s, 3H); 1.62 (m, 1H); 1.45 (m, 1H); 1.33 (m, 1H); 1.2–1.1 (m, 2H); 0.85 (m, 1H). ^{13}C NMR (50.32 MHz) 137.72, 130.65, 114.84, 114.78, 80.53, 42.42, 37.13, 31.49, 28.41, 27.92, 24.05, 21.64. IR ν/cm^{-1} 3100, 2995, 1650, 1610, 1070.



Scheme 1 *Reagents and conditions*: i, $H_2C{=}C(Me)C{\equiv}CCH_2OH$, NBS (−15 °C, 3 h); ii, $\mathrm{Bu^tOK}$ (1.3 equiv.), benzene, reflux, 2 h; iii, DBU (3 equiv., 110 °C, 3 h); iv, $\mathrm{Bu^tOK}$ (0.3 equiv., pentane, reflux, 0.5–2 h; v, MeOH, camphorsulfonic acid (CSA) 3%, 2 h; vi, Jones' reagent

tion of the acetylenic unit,[5] leading to β-bromovinyl allenyl ethers **4a, b** (65–67%) and then to **6a, b** (78–82%), upon treatment with DBU. This base-catalysed isomerization into a vinylallenyl moiety accounts for the clean intramolecular cycloaddition of **3**. The structures of [4 + 2] cycloaddition adducts **6** were confirmed by selective conversion into acetals **7** and the corresponding polycyclic fused lactones **8**, the structures of which constitute the framework of a number of natural terpenes.[6]

In conclusion, the base-promoted consecutive dehydrobromination–isomerization–intramolecular cycloaddition of readily available derivatives **2** provides a selective means for the functionalization of cycloalkenes **1** into tricyclic structures **6** with high synthetic potential.

Received, 9th November 1992; Com. 2/05958D

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