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LETTERS

Vinylidene to alkyne rearrangement to form polyynes: synthesis and photolysis of dialkynylmethylenebicyclo[4.3.1]deca-1,3,5-triene derivatives

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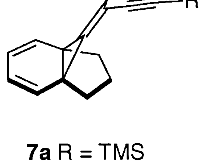
Abstract—Dialkynylmethylenebicyclo[4.3.1]deca-1,3,5-triene derivatives were synthesized as precursors to generate dialkynylvinylidenes by extrusion of an aromatic fragment, indane. Photolysis of the trienes gave linear polyynes as the major products produced by rearrangement of the vinylidenes, together with the isomerization products having a methylenecycloheptatriene moiety. © 2001 Elsevier Science Ltd. All rights reserved.

In connection with the formation of novel, conjugated polyynes such as cyclo[*n*]carbons,[1] there has been considerable interest in the development of methods to generate polyynes under unconventional, mild conditions. These include retro Diels–Alder reaction of dibenzobicyclo[2.2.2]octatriene derivatives,[2] decarbonylation of cyclobutenedione derivatives,[2b,3] retro [2+2] fragmentation of cyclobutene-containing propellanes,[4] and others.[5] Similarly, in order to generate diethynylcarbene, which is a repeating unit of cyclo[5*n*]carbons, cheletropic fragmentation of cyclopropane-containing propellanes has been investigated under mass spectrometric conditions.[6] As a new, alternative method, we planned to utilize the vinylidene to alkyne rearrangement[7] of dialkynylvinylidenes to form reactive, conjugated polyynes. Recently, Tykwinski reported an ingenious use of the rearrangement of vinylidene carbenoids generated from dialkynyldibromoalkenes,[8] known as the Fritsch–Buttenberg–Wiechell rearrangement,[9] leading to the efficient formation of polyynes. By contrast, as precursors to dialkynylvinylidenes, we designed dialkynylmethylenebicyclo[4.3.1]deca-1,3,5-trienes, which would produce dialkynylvinylidenes by extrusion of an aromatic fragment (indane) presumably via the corresponding propelladiene valence isomers. The preceding observations underlying our design are following: (1) Thermally induced fragmentation of dihalomethano[10]annulenes has been reported to form dihalocarbenes by elimination of naphthalene,[10] although the mechanism, whether or not the corresponding [4.4.1]propellatetraene is involved, is not clear.[10b] (2) Photolysis of cyclopropane-containing propellanes has been recognized as a method to form 'real carbenes',[11] including such peculiar species as homocubylidene.[11c] (3) Photolysis of alkylidenecyclopropane derivatives produced alkylidene carbenes which either rearranged to alkynes or were trapped by olefins.[12] Herein, we report the synthesis of dialkynylmethylenebicyclo[4.3.1]decatriene derivatives **1a** and **2** and their photolysis forming the corresponding polyynes.

The synthesis of the vinylidene precursors **1a** and **2** was carried out as outlined in Scheme 1. Dibromo[4.3.1]propellene **3**, prepared by dibromocarbene addition to dihydroindane,[13] was converted to the propelladiene **4**[11b,d,e] by bromination–dehydrobromination. Halogen–lithium exchange of **4** followed by treatment of diethynyl ketone **5** and TMSCl gave adduct **6** as a single diastereomer. Treatment of **6** with *t*-BuLi gave methylenebicyclotriene **1a** by Peterson type elimination[14] and subsequent ring opening of the three-membered ring. Apparently, the open form **1a** having a bridged methylenecycloheptatriene structure is more stable than the closed isomer **7a** with a propelladiene form.[15] After removal of the TMS group, the resulting **1b** was coupled with bromoalkyne **8** to give butadiynyl derivative **2**.



7a R = TMS
7b R = H

Keywords: vinylidene; alkynes; polyynes; photolysis.

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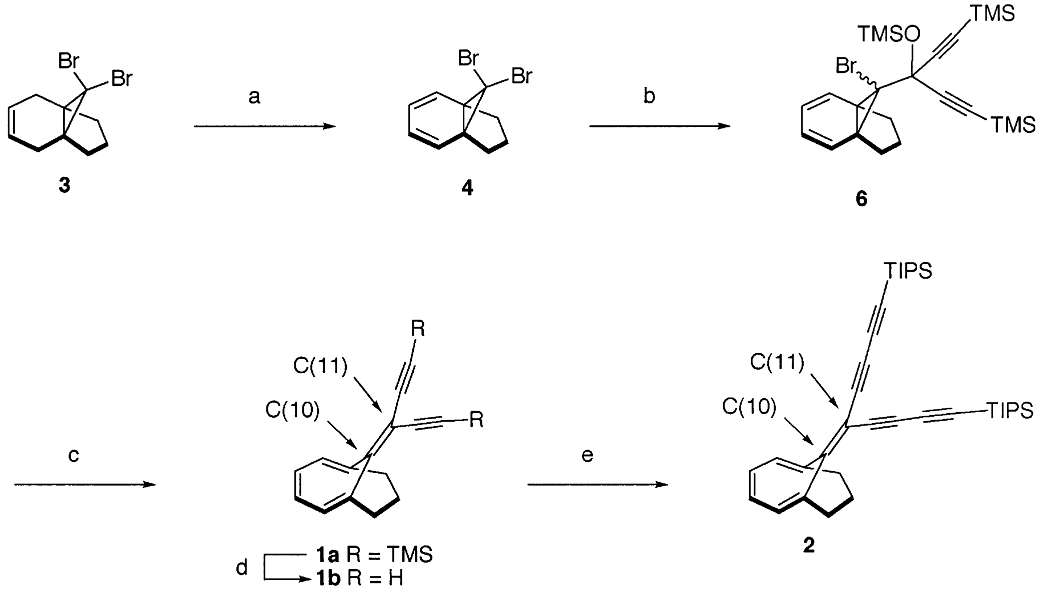
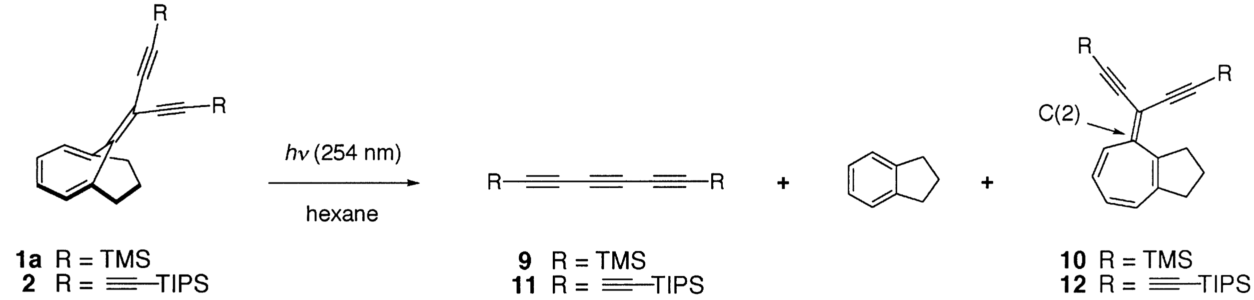
The ^{13}C NMR spectra of **1a**, **1b** and **2** exhibit characteristic chemical shifts due to polarization of the exocyclic double bond. Namely, the signals for C(10) of **1a**, **1b** and **2** shift remarkably low field to 167.0, 168.0, and 171.9 ppm, respectively, which are even lower than that of dicyanomethylenecycloheptatriene (163.7 ppm).[16] By contrast, the signals for C(11) of **1a**, **1b** and **2** appear upfield at 93.1, 90.8, and 91.2 ppm, respectively. These observations are explained in terms of the electronic polarization of the double bond due to the electron-withdrawing effect of the ethynyl group and to the steric effect imposed by the bridged bicyclic system. For example, it has been reported by Itô that the chemical shifts of the carbonyl carbons of 2,7-methylene-bridged tropones shift low field with decreasing length of the methylene bridge presumably due to bond angle strain.[17] The effect of the non-planar structure of **1a** and **2** is also evidenced by their electronic spectra [**1a** λ_{max} (hexane) 258 nm (ε 16500), **2** λ_{max} (hexane) 306 (ε 19600), 288 (19200), 269 (15400), 256 (13300) nm], which do not exhibit an absorption in the visible region (around 400 nm) characteristic of the heptafulvene chromophore.[18] This indicates that the exocyclic double bond is not fully conjugated with the bridged triene system due to the out-of-plane bending of the double bond.

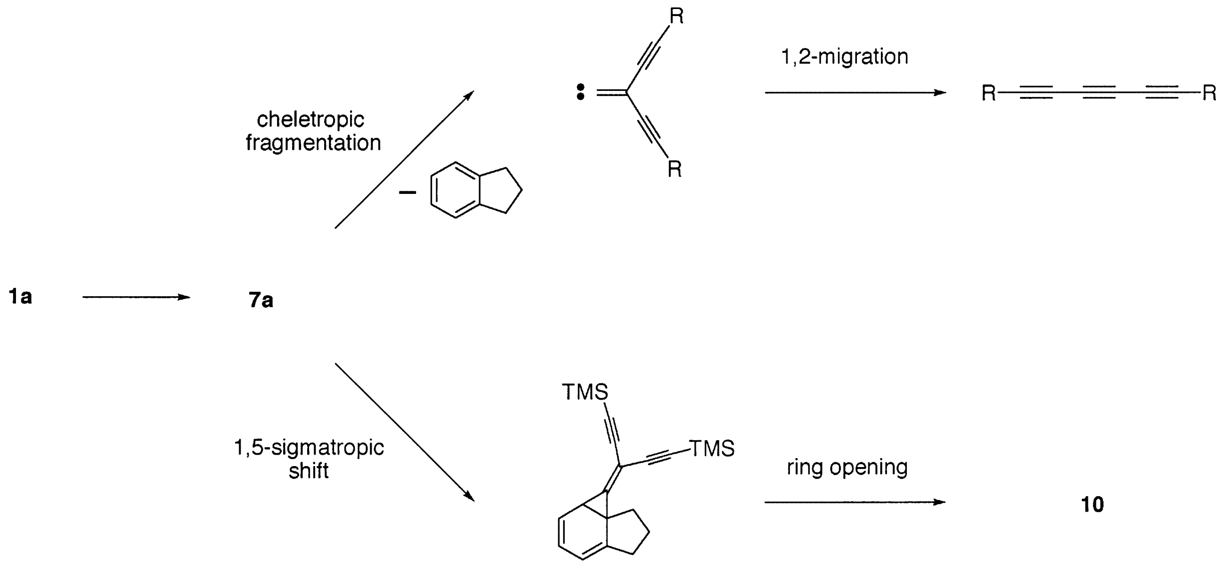
Irradiation of a hexane solution of **1a** with a low pressure mercury lamp in an ice bath yielded hexatriyne **9**[19] as the major product as we had expected, which was isolated in 46% yield after chromatography together with indane (45% yield determined by GLC).[20] In addition, the isomerization product **10** of the starting material was obtained in 30% yield as a brown oil (Scheme 2). The structure of **10** was elucidated on the basis of the NMR and UV–vis spectra. The salient features of the NMR spectra include four vinyl proton signals at 6.90 (d, 1H), 6.37 (dd, 1H), and 6.21–6.12 (m, 2H) ppm and six vinyl carbon signals at 151.3, 145.1, 144.9, 134.4, 132.0, 130.5, 128.7, and 93.5 ppm. It should be pointed out that, although the ^{13}C NMR chemical shifts of the exocyclic double bond of **10** indicate its polarization as in the case of **1a**, the chemical shift for C(2) is not as much downfield shifted as that of **1a**,



Scheme 1. (a) (i) $C_5H_5N\cdot HBr_3$, C_5H_5N, CH_2Cl_2, rt; (ii) DBU, toluene, 42°C, 35%; (b) BuLi, −100°C, then (TMS-C≡C)$_2$C=O (**5**), −70°C, then TMSCl, THF, 46%; (c) *t*-BuLi, pentane, −110°C, then TMSCl, 80%; (d) LiOH·H_2O, THF, rt, 78%; (e) TIPS-C≡C-Br (**8**), CuCl, $NH_2OH\cdot HCl$, aq. $EtNH_2$, THF–MeOH (1:2), rt, 63%.



Scheme 2.



Scheme 3.

implying the presence of steric effect in the latter. The UV–vis spectrum of **10** (hexane) exhibits a strong absorption at 385 nm (ε 3300) consistent with the heptafulvene chromophore.[18] The formation of **10** can be explained in terms of a 1,5-sigmatropic shift of a cyclopropane bond of the propelladiene intermediate **7a**, the valence isomer of **1a**, followed by electrocyclic ring opening of the norcaradiene moiety (Scheme 3).

Irradiation of the extended system **2** under similar conditions gave decapentayne **11**[19c,d] in 59% isolated yield together with isomerization product **12** (ca. 24%). Indane was also detected by GLC and ^{1}H NMR (irradiation in THF-d_8). Thus, despite the formation of undesired isomerization products, generation of vinylidenes and subsequent isomerization to polyynes took place as the major course of the photoreaction of the methylenebicyclo[4.3.1]decadienes. Preparation and fragmentation of cyclic oligomers of **1b** are being undertaken in these laboratories and will be reported in due course.

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