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Photochemical Method for Generation of Linear Polyynes: [2 + 2] Cycloreversion of [4.3.2]Propellatrienes Extruding Indan

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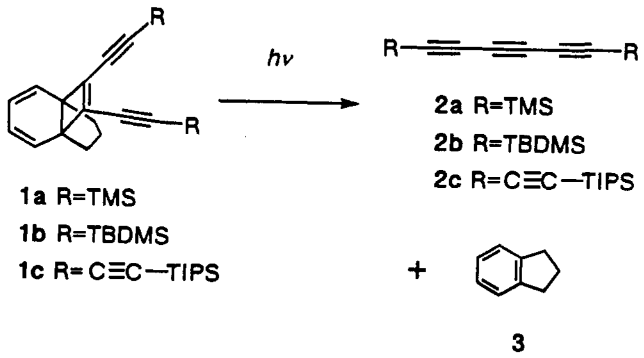
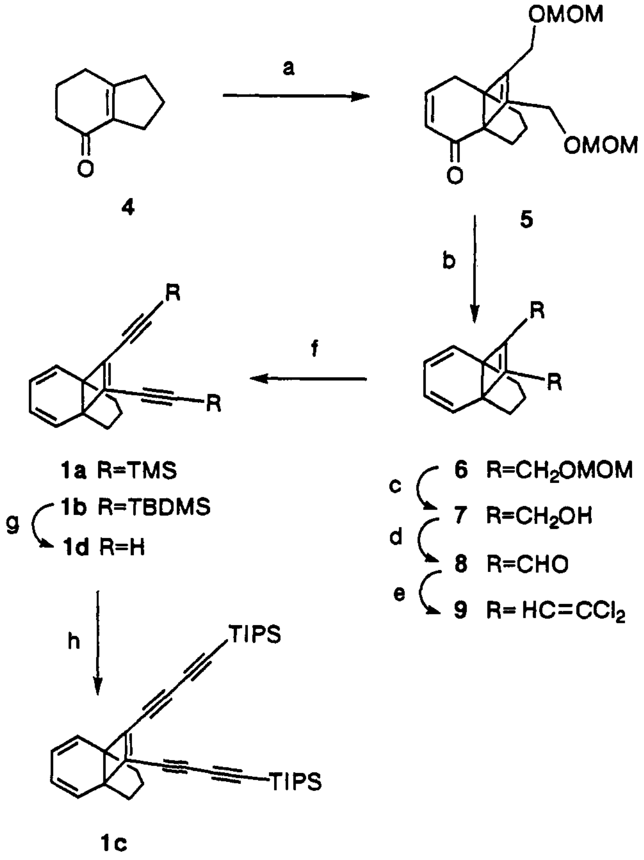
Summary: Photolysis of trienediynes **1a** and **1b** and trienetetrayne **1c** having a [4.3.2]propellane framework yielded the respective linear polyynes **2a–c** in good efficiency through [2 + 2] cycloreversion, extruding indan (**3**).

Recently, enormous interest has been shown in conjugated cyclic acetylenes from new aspects such as biologically (antitumor) active compounds,[1a] precursors for strained molecules,[1b] and new carbon clusters.[1c] In general, cyclic acetylenes become increasingly unstable as the ring size decreases or the degree of unsaturation increases. In order to produce such high-energy species, a thermal or photochemical extrusion reaction from suitable substrates is particularly promising. Indeed, thermal extrusion of carbon monoxide has been examined by Diederich to generate monocyclic carbon cluster molecules (cyclo[*n*]-carbons).[1c,2] Photochemical [2 + 2] cycloreversion from cyclobutane precursors, on the other hand, has been successfully utilized to produce highly unstable molecules with carbon–carbon double bonds such as cyclobutadiene[3] and Dewar furan.[4] However, the corresponding reaction of cyclobutene derivatives, which generate a carbon–carbon triple bond, has been scarcely known; the only example reported by Paquette is that of [4.4.2]propellatriene and -tetraene which on photolysis gave acetylene along with tetralin and naphthalene, respectively.[5] In order to develop a general photochemical method to generate a carbon–carbon triple bond by [2 + 2] cycloreversion, we designed, as a model system, the [4.3.2]propellatriene derivatives **1a–c** which would produce linear polyynes **2a–c**, extruding indan (**3**) (Scheme 1).[6,7] In this connection, we report here the synthesis and photochemical reactions of the propellanes **1a–c**.

Scheme 1



Scheme 2[a]



[a] Key: (a) (i) $MOMOCH_2C{\equiv}CCH_2OMOM$, *hν*, Pyrex, CH_2Cl_2, 70%; (ii) TMSOTf, Et_3N, CCl_4; (iii) $Pd(OAc)_2$, CH_3CN, 53% for two steps; (b) (i) $NaBH_4$, $CeCl_3{\cdot}7H_2O$, MeOH; (ii) $C_6H_3(NO_2)_2SCl$, Et_3N, $ClCH_2CH_2Cl$, 84% for two steps; (c) aqueous HCl, THF, 68%; (d) MnO_2, CH_2Cl_2, 78%; (e) $CCl_3PO(OEt)_2$ (12 equiv), BuLi (10 equiv), THF, −100 °C, 64%; (f) BuLi (5.5 equiv), THF, −78 °C, then TMSCl for **1a** (78%) or TBDMSCl for **1b** (47%); (g) TBAF, wet THF, 78%; (h) $BrC{\equiv}CTIPS$ (3.0 equiv), CuCl (0.4 equiv), $EtNH_2$ (15 equiv), $NH_2OH{\cdot}HCl$ (3.2 equiv), MeOH/THF (2:1), 95%.

First, trienediynes **1a** and **1b** were prepared according to Scheme 2. Photocycloaddition of enone **4**[8] with the bis-MOM ether[9] of 2-butyne-1,4-diol followed by dehy-

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(7) For a thermal extrusion method of carbon monoxide generating linear polyynes:[2] Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943.

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drogenation[10] through the corresponding silyl enol ether gave enone **5**. This was converted to triene **6** by hydride reduction and subsequent 1,4-elimination.[11] Deprotection of **6** gave diol **7** which was oxidized by MnO_2 to yield dialdehyde **8**. Conversion of **8** to tetrachloro olefin **9** was accomplished using a large excess (12 equiv) of diethyl (trichloromethyl)phosphonate and BuLi (10 equiv).[12] Treatment of **9** with BuLi followed by quenching with TMSCl or TBDMSCl gave trienediyne **1a** or **1b**. Irradiation of a hexane solution of **1a** in a quartz tube with a low-pressure mercury lamp yielded the hexatriyne **2a**[7,13] in 66% isolated along with indan (**3**). A small amount (ca. 13% by GLC) of an unidentified product was also formed.[14] Similar photolysis of **1b** afforded the triyne **2b**[7] in 67% isolated yield together with an unidentified byproduct (11% by GLC).[14]

Next, trienetetrayne **1c** was prepared from unstable hydrocarbon **1d**, which was obtained by deprotection of **1b**, by the Cadiot–Chodkiewicz coupling[15] with a TIPS-protected bromoacetylene[7] (Scheme 2). Finally, irradiation of **1c** under the similar conditions yielded the decapentayne **2c**[7] in 74% isolated yield.

In symmary, [2 + 2] cycloreversion of propellatrienes **1a–c** proceeded as the major pathway of the photolysis, giving the linear polyynes **2a–c**. Applications of this method to the synthesis of cyclic polyynes as well as other unsaturated labile molecules are in progress in our laboratories.

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Supplementary Material Available: Listing of spectral properties and ^1H and ^{13}C NMR of spectra **1a–d** and **5–9** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) The unidentified products derived from **1a** and **1b** might be derived by di-π methane or other skeletal rearrangement since they have GLC retention times and molecular weights similar to those of the starting materials. Irradiation of **1a** and **1b** with a high-pressure mercury lamp through a Pyrex filter gave slightly larger amount of these unidentified products.

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