Facile Synthesis of [3]Cumulenes via 1,4-Elimination of Hydroxytrimethylsilane from 4-(Trimethylsilyl)-2-butyn-1-ols[1]

Kung K. Wang,* Bin Liu, and Yong-de Lu

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506

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The DNA-cleaving activity of neocarzinostatin (NCS) and the mechanism of the cleavage action have received much attention in recent years.[2] It is proposed that the nonprotein chromophore of neocarzinostatin (NCS-Chrom) undergoes an initial transformation to a cyclic enyne[3]cumulene followed by the formation of a carbon biradical species. The resulting biradical is believed to be responsible for hydrogen atom abstraction from the sugar phosphate backbone of the DNA, causing the subsequent oxidative cleavage and producing the potent cytotoxicity of neocarzinostatin.[3] The participation of a [3]cumulene moiety in the biradical formation step of the NCS-Chrom together with the interesting chemical reactivities of [3]cumulenes[4] have stimulated interest in developing synthetic routes to [3]cumulenes.[4,5] A recent report by Chow et al. concerning a facile synthesis of [3]-cumulenes via tetrabutylammonium fluoride (TBAF)-induced 1,4-eliminations of 1-acetoxy-4-(trimethylsilyl)-2-butynes[5a] prompted us to disclose a full account of our independent findings in this area.[1]

Scheme 1

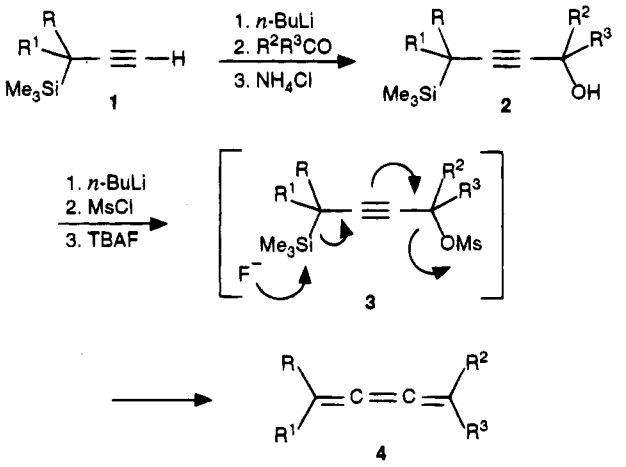

Table 1. Synthesis of 4-(Trimethylsilyl)-2-butyn-1-ols 2 and [3]Cumulenes 4

1	aldehyde or ketone	2, isolated yield, %	4, yield,[b] % (isolated yield, %)
R = H, R¹ = *n*-Bu	R² = H, R³ = *n*-Bu	**2a**, 81[a]	**4a**, 61[c]
R = H, R¹ = *n*-Bu	R² = Me, R³ = Me	**2b**, 68	**4b**, 70 (48)
R = H, R¹ = *n*-Bu	R² = H, R³ = Ph	**2c**, 84[a]	**4c**, 68 (45)[c]
R = H, R¹ = Ph	R² = H, R³ = *n*-Bu	**2d**, 78[a]	**4c**, 84[c]
R = H, R¹ = Ph	R² = Me, R³ = Me	**2e**, 80	**4e**, 71
R = Me, R¹ = Me	R² = H, R³ = Ph	**2f**, 95	**4e**, 83
R = Me, R¹ = Me	R² = H, R³ = *n*-Bu	**2g**, 80	**4b**, 84
R = Me, R¹ = Me	R², R³ = $-(CH_2)_5-$	**2h**, 63	**4h**, 52
R = H, R¹ = H	R², R³ = $-(CH_2)_5-$	**2i**, 60	**4i**, 53
R = H, R¹ = H	R² = H, R³ = Ph	**2j**, 81	**4j**[d]

[a]The isolated product contains a 1:1 mixture of two diastereomeric isomers. [b]The yield of the reaction was determined by comparison of the integrated peak areas of the ^{1}H NMR signals using 1,4-dibromobenzene as the internal standard. [c]The product contains a 1:1 mixture of the *E* and the *Z* isomers. [d]The formation of **4j** was not detected by GC/MS.

Treatment of propargylic trimethylsilane **1**,[6] readily prepared from the corresponding terminal alkyne, 3-methyl-1-butyn-3-ol, or 3-bromo-1-propyne, in THF with *n*-butyllithium followed by condensation with an aldehyde or a ketone afforded 4-(trimethylsilyl)-2-butyn-1-ol **2** (Scheme 1) in good yields (Table 1).[7] In the cases of **2a**, **2c**, and **2d**, essentially equal amounts of two diastereomeric isomers were formed. Sequential treatment of **2** with *n*-butyllithium, methanesulfonyl chloride, and TBAF furnished the corresponding [3]cumulene **4** (Table 1). Apparently, the reaction proceeds through the formation of methanesulfonate **3**, which then undergoes a 1,4-elimination reaction via the pathway of selectively attacking the trimethylsilyl group by the fluoride ion leading to **4** (Scheme 1).[8] Because of the lack of diastereomeric purity in the cases of **2a**, **2c**, and **2d**, [3]-

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cumulenes **4a** and **4c** contain essentially equal amounts of the *E* and the *Z* isomers.

The [3]cumulenes **4** listed in Table 1 are in general sensitive to oxygen and were found to polymerize rapidly when stored in high concentrations at room temperature. Attempts to isolate **4** by column chromatography (Florisil/pentane) resulted in the formation of significant amounts of polymeric materials in several cases. Fortunately, in most cases [3]cumulenes **4** were stable enough to allow detection by GC/MS, and a small portion of **4** in high enough purity could be isolated by column chromatography to allow structural elucidation. The efficiency of conversion of **2** to **4** was determined by comparison of the integrated peak areas of the ^{1}H NMR signals of the crude reaction products using 1,4-dibromobenzene as an internal standard. However, in the case of **4j** although all of the starting alcohol **2j** was completely reacted as indicated by following the reaction with GC/MS, the corresponding monosubstituted [3]cumulene **4j** was not detected. Presumably, **4j** was formed initially but was too unstable under the reaction conditions and decomposed rapidly to polymeric materials even in dilute solution. The monosubstituted [3]cumulenes are known to be thermally unstable and form polymeric materials rapidly at room temperature.[5c] Likewise, the lower conversion efficiency in the case of **4a** could also be attributed to its low thermal stability.[5l] In the cases of **4h** and **4i**, substantial amounts of unreacted starting alcohols **2h** and **2i** were present in the reaction mixtures.

It is worth noting that conversion of **2** to **4** could also provide a rare opportunity to study the stereochemistry of the 1,4-elimination reaction. Since the precursors **2a**, **2c**, and **2d** are mixtures of diastereomers and the resulting [3]cumulenes are 1:1 mixtures of the *E* and the *Z* isomers, the preference of the reaction pathway in proceeding through either syn- or anti-elimination or no preference at all could not be determined at the present time. As in the cases of 1,2-elimination of β-hydroxyalkylsilanes under acidic or basic conditions,[9] a definitive answer regarding the stereochemistry of the 1,4-elimination step will require the preparation of a diastereomerically pure 4-(trimethylsilyl)-2-butyn-1-ol and the determination of the relative stereochemical relationship of the two chiral centers.

In conclusion, the reaction sequence outlined in Scheme 1 could be easily adopted for the synthesis of [3]cumulenes with diverse chemical structures by selecting different combinations of aldehydes or ketones for condensation with propargylic trimethylsilanes to produce 4-(trimethylsilyl)-2-butyn-1-ols as precursors. Examples listed in Table 1 consist of 1,1- and 1,4-disubstituted as well as tri- and tetrasubstituted [3]cumulenes. The monosubstituted [3]cumulenes presumably could also be generated in situ by this procedure. The use of this synthetic method for the preparation of a variety of [3]-cumulenes for subsequent synthetic elaborations, including the preparation of enyne[3]cumulenes from enynyl aldehydes and ketones for generating the corresponding biradicals, is being investigated.

Experimental Section

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. *n*-Butyllithium (2.5 M) in hexanes, methanesulfonyl chloride, TBAF, and 3-(trimethylsilyl)-1-propyne[6d] were purchased from Aldrich Chemical Co., Inc., and were used as received. 3-(Trimethylsilyl)-1-heptyne, 3-(trimethylsilyl)-3-phenyl-1-propyne, and 3-methyl-3-(trimethylsilyl)-1-butyne were prepared according to the reported procedures.[6] 4-(Trimethylsilyl)-2-butyn-1-ols **2i** and **2j** were also synthesized according to the reported procedures.[7] To ensure accuracy of the yields of [3]cumulenes determined by comparison of the integrated peak areas of the ^{1}H NMR signals using 1,4-dibromobenzene as the internal standard, the acquisition parameters of the NMR spectrometer were set to have a long acquisition time (5 s) and pulse delay (5 s). The ^{1}H NMR spectrum of a sample of 1-nonene and 1,4-dibromobenzene in C_6D_6, prepared under a nitrogen atmosphere, was recorded using these identical acquisition parameters. The accuracy of the integrated peak areas was found to be greater than 95%.

8-(Trimethylsilyl)-6-dodecyn-5-ol (2a). The following procedure for the preparation of **2a** is representative for the synthesis of 4-(trimethylsilyl)-2-butyn-1-ols. To a solution of 0.86 g of 3-(trimethylsilyl)-1-heptyne (5.1 mmol) in 10 mL of dry THF under a nitrogen atmosphere at −50 °C was added by a syringe 2.0 mL of a 2.5 M solution of *n*-butyllithium (5.0 mmol) in hexanes. After 25 min of stirring at −50 °C, 0.53 mL of pentanal (0.43 g, 5.0 mmol) was added by a syringe and the reaction mixture was allowed to warm to rt before 30 mL of pentane and 15 mL of a 10% NH_4Cl solution were introduced. The organic layer was separated and washed with water (3 × 20 mL), and the combined aqueous layers were extracted with pentane (2 × 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (silica gel/5% diethyl ether in hexanes) to furnish 1.03 g of **2a** (81% yield, 1:1 mixture of two diastereomeric isomers) as a colorless liquid: IR (neat) 3346, 2216, 1249, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.37 and 4.36 (1 H, t, J = 6.6 Hz), 1.80 (1 H, OH), 1.7−1.5 (3 H, m), 1.45−1.2 (10 H, m), 0.90 (3 H, t), 0.89 (3 H, t), 0.06 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 87.46, 87.43, 81.97, 81.93, 62.97, 38.17, 31.85, 31.84, 28.78, 28.77, 27.48, 27.45, 22.39, 22.33, 19.71, 19.69, 14.04, 13.98, −3.20; MS *m/e* 236 (M^+ − H_2O), 209, 164, 73.

2-Methyl-5-(trimethylsilyl)-3-nonyn-2-ol (2b): colorless liquid; IR (neat) 3362, 2220, 1249, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.97 (1 H, br s, OH), 1.58−1.52 (2H, m), 1.47 (6 H, s), 1.4−1.2 (5 H, m), 0.88 (3 H, t), 0.04 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 85.79, 84.52, 65.46, 31.98, 31.82, 28.70, 22.33, 19.48, 13.97, −3.24; MS *m/e* 208 (M^+ − H_2O), 183, 73.

4-(Trimethylsilyl)-1-phenyl-2-octyn-1-ol (2c): light yellow liquid; 1:1 mixture of two diastereomeric isomers; IR (neat) 3364, 2216, 1249, 838, 753, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.55 (2 H, d), 7.4−7.28 (3 H, m), 5.48 (1 H, s), 2.02 (1 H, br s, OH), 1.7−1.5 (2 H, m), 1.5−1.2 (5 H, m), 1.35 (3 H, t), 0.08 and 0.07 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 141.81, 141.79, 128.38, 127.99, 127.97, 126.68, 126.64, 89.91, 80.63, 80.59, 65.03, 31.94, 28.76, 22.35, 19.94, 14.01, −3.08; MS *m/e* 256 (M^+ − H_2O), 179, 153, 141, 107, 73. Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55. Found: C, 74.25; H, 9.82.

1-(Trimethylsilyl)-1-phenyl-2-octyn-4-ol (2d): light yellow liquid; 1:1 mixture of two diastereomeric isomers; IR (neat) 3372, 2218, 1249, 843 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.3−7.1 (5 H, m), 4.46 (1 H, m), 3.16 and 3.15 (1 H), 2.3 (1H, br, OH), 1.8−1.65 (2 H, m), 1.55−1.30 (4 H, m), 0.92 (3 H, t), 0.04 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 139.19, 139.17, 128.16, 126.95, 125.14, 85.32, 85.31, 84.02, 84.00, 63.02, 62.98, 38.07, 29.36, 29.32, 27.51, 22.42, 14.06, −3.25; MS *m/e* 256 (M^+ − H_2O), 241, 184, 73. Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55. Found: C, 74.23; H, 9.47.

2-Methyl-5-(trimethylsilyl)-5-phenyl-3-pentyn-2-ol (2e): yellow liquid; IR (neat) 3383, 2224, 1249, 843, 756, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.3−7.1 (5 H, m), 3.12 (1 H, s), 2.6 (1 H, br, OH), 1.563 (3 H, s), 1.555 (3 H, s), 0.04 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 139.20, 128.13, 126.87, 125.09, 87.99, 82.44, 65.54, 31.91, 31.84, 29.06, −3.29; MS *m/e* 228 (M^+ − H_2O), 188, 156, 141, 115, 73.

4-Methyl-4-(trimethylsilyl)-1-phenyl-2-pentyn-1-ol (2f): light yellow liquid; IR (neat) 3382, 2221, 1249, 840, 750, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.53 (2 H, dd, J = 7.4 and 1.6 Hz), 7.39−7.29 (3 H, m), 5.46 (1 H, d, J = 5.9 Hz), 2.25 (1 H, d, J = 5 Hz), 1.19 (6 H, s), 0.06 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 141.65, 128.37, 127.97, 126.61, 95.06, 79.75, 64.87, 23.92, 23.89, 17.11, −4.46; MS *m/e* 228 (M^+ − H_2O), 213, 159, 73.

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2-Methyl-2-(trimethylsilyl)-3-nonyn-5-ol (2g): colorless liquid; IR (neat) 3354, 2220, 1249, 843 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.36 (1 H, t, J = 6.6 Hz), 1.68–1.6 (2 H, m), 1.63 (1 H, s, OH), 1.45–1.3 (4 H, m), 1.14 (6 H, s), 0.91 (3 H, t), 0.06 (9 H, s); MS m/e 208 ($M^+ - H_2O$), 193, 140, 125, 73.

1-[3-Methyl-3-(trimethylsilyl)-1-butynyl]cyclohexanol (2h): white solid; IR (neat) 3371, 2226, 1249, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.93 (1 H, br s, OH), 1.9–1.8 (2 H, m), 1.7–1.6 (2 H, m), 1.6–1.45 (6 H, m), 1.13 (6 H, s), 0.06 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 92.23, 83.58, 68.95, 40.56, 25.31, 24.14, 23.64, 16.83, −4.03; MS m/e 220 ($M^+ - H_2O$), 171, 140, 73.

5,6,7-Dodecatriene (4a).[5i] The following procedure for the preparation of **4a** is representative for the synthesis of [3]-cumulenes from **2**. To a solution of 0.508 g of **2a** (2.0 mmol) (and 0.174 g of anhydrous LiBr in the cases of tertiary alcohols) in 6 mL of THF under a nitrogen atmosphere at −70 °C was added dropwise by a syringe 0.84 mL of a 2.5 M solution of n-butyllithium (2.1 mmol) in hexanes. After 30 min of stirring at −70 °C, a solution of 0.241 g of methanesulfonyl chloride (2.1 mmol) in 3 mL of THF was introduced via cannula. The reaction mixture was stirred at −70 °C for an additional 1 h before 6 mL of a 1.0 M solution of TBAF in THF (8 mL in the cases of tertiary alcohols) was introduced. The reaction mixture was then allowed to warm to 0 °C. After 30 min, the reaction mixture was transferred via cannula to a separatory funnel containing a cold solution of 15 mL of a degassed aqueous Na_2CO_3 solution and 50 mL of pentane under a nitrogen atmosphere. The aqueous layer was separated, and the organic layer was washed with 10 mL of a degassed Na_2CO_3 solution and 10 mL of degassed water. The organic layer was then transferred via cannula to a flask and was concentrated under reduced pressure to ca. 2 mL in total volume at 0 °C. A solution of 0.222 g of 1,4-dibromobenzene (0.94 mmol) in 2 mL of C_6D_6 was then introduced, and the yield of **4a** (61%) was determined by comparison of the integrated peak areas of the ^1H NMR signals of 1,4-dibromobenzene at δ 6.77 and the vinylic hydrogens of **4a** at δ 5.49 and 5.48. The starting **2a** was found to be completely reacted. In a second run, the concentrated crude [3]-cumulene was purified by column chromatography (Florisil, 100–200 mesh, Fisher F-101, pentane) under a nitrogen atmosphere at 0 °C. Pentane was then evaporated at 0 °C, and the spectral data of **4a** (1:1 mixture of the E and the Z isomers) were promptly recorded: ^1H NMR (C_6D_6) δ 5.49 and 5.48 (2 H, tm, J = 5 and 1 Hz), 2.10 (4 H, q, J = 6 Hz), 1.45–1.30 (4 H, m), 1.30–1.15 (4 H, m), 0.82 (3 H, t, J = 7.1 Hz), 0.80 (3 H, t, J = 7.1 Hz); ^{13}C NMR (C_6D_6) δ 162.04, 161.94, 107.76, 107.64, 32.79, 32.74, 31.31, 31.15, 22.49, 14.08, 14.05; MS m/e 164 (M^+), 135, 121, 107.

2-Methyl-2,3,4-nonatriene (4b): colorless liquid; ^1H NMR (C_6D_6) δ 5.35 (1 H, t of septet, J = 7.2 and 1.3 Hz), 2.13 (2 H, qm, J = 7.3 and 1 Hz), 1.74 (3 H, m, J = 1 Hz), 1.72 (3 H, m, J = 1 Hz), 1.47–1.3 (2 H, m), 1.3–1.2 (2 H, m), 0.83 (3 H, t); ^{13}C NMR (C_6D_6) δ 158.94, 157.26, 111.78, 103.39, 32.53, 31.51, 24.28, 23.89, 22.50, 14.08; MS m/e 136 (M^+), 121, 107, 93, 91, 80, 79, 77.

1-Phenyl-1,2,3-octatriene (4c): colorless liquid; 1:1 mixture of the E and the Z isomers; ^1H NMR (C_6D_6) δ 7.42 and 7.37 (2 H, d, J = 7 Hz), 7.10 (2 H, tm, J = 5.5 and 1.5 Hz), 6.99 (1 H, tm, J = 7 and 1 Hz), 6.36 (d, J = 1.5 Hz) and 6.33 (d, J = 1 Hz) (1 H), 5.62 (q, J = 7.4 Hz) and 5.54 (q, J = 7.3 Hz) (1 H), 2.12 (2 H, q, J = 7.2 Hz), 1.5–1.3 (2 H, m), 1.3–1.2 (2 H, m), 0.83 (3 H, t); ^{13}C NMR (C_6D_6) δ 160.35, 160.08, 159.48, 159.44, 137.57, 137.42, 128.87, 127.88, 127.79, 127.75, 111.64, 111.60, 107.30, 107.22, 33.32, 32.92, 31.18, 31.09, 22.49, 22.44, 14.05, 14.04; MS m/e 184 (M^+), 169, 155, 141, 128, 115, 77.

4-Methyl-1-phenyl-1,2,3-pentatriene (4e): colorless liquid; IR (neat) 2050 cm^{-1}; ^1H NMR (C_6D_6) δ 7.41 (2 H, d, J = 7 Hz), 7.13 (2 H, t, J = 7 Hz), 6.99 (1 H, t, J = 7 Hz), 6.25 (1 H, s), 1.76 (3 H, s), 1.71 (3 H, s); ^{13}C NMR (C_6D_6) δ 157, 155, 137.99, 128.84, 127.48, 127.18, 116.84, 103.50, 24.95, 24.00; MS m/e 156 (M^+), 141, 128, 115, 77.

4-Methyl-1,1-pentamethylene-1,2,3-pentatriene (4h):[5h] white solid; ^1H NMR (C_6D_6) δ 2.26 (4 H, t, J = 6 Hz), 1.78 (6 H, t, J = 0.8 Hz), 1.48 (4 H, quintet, J = 6 Hz), 1.33 (2 H, m); ^{13}C NMR (C_6D_6) δ 155.25, 151.91, 115.77, 107.44, 35.10, 28.09, 26.33, 24.02; MS m/e 148 (M^+), 133, 119, 105, 91.

1,1-Pentamethylene-1,2,3-butatriene (4i): ^1H NMR (C_6D_6) δ 4.93 (2 H, quintet, J = 1.0 Hz), 2.16 (4 H, t, J = 6.5 Hz), 1.39 (4 H, quintet, J = 6 Hz), 1.2 (m); MS m/e 120 (M^+), 105, 91, 79, 77.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of **2a-h** and **4a-i** (26 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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