110 and 2800 we report here for the cubyl system.[14] These large rate enhancements are more like those obtained by Adcock and Shiner et al. for the solvolysis of Si- and Sn-bridgehead-substituted 1-bicyclo[2.2.2]octyl mesylates, wherein σ-donation from the metalloid substituent is thought to enhance double hyperconjugation.[13,15] Even so, this charge delocalization mechanism is probably unimportant for cubyl cation.[6] Unlike the bicyclooctyl case where ring cleavage is pronounced, careful NMR analysis reveals no opening of the cubane cage in the course of the solvolysis of 4-(trimethylstannyl)cubyl mesylate. The delocalization described by Hrovat and Borden's ab initio calculations rationalizes the available observations for cubyl cation more than adequately.

Acknowledgment. This work was funded in part by the National Science Foundation (CHE-9010059). We are grateful to Prof. Borden for many invigorating conversations and for a preprint of his manuscript on double hyperconjugation.

Registry No. 1, 125665-92-1; **2**, 111873-46-2; **3a**, 139427-87-5; **3b**, 139427-88-6; **4**, 139427-89-7; **5a**, 139427-90-0; **5a** alcohol, 139427-91-1; **5b**, 139427-92-2; **5b** alcohol, 139427-93-3; cubyl triflate, 125762-86-9; 4-methylcubyl triflate, 125762-87-0; 4-chlorocubyl triflate, 125762-90-5; 4-methoxycubyl triflate, 139427-94-4; 4-trimethylsilylcubyl acetate, 139427-95-5; 4-trimethylstannylcubyl acetate, 139427-96-6; 4-trimethylstannylcubyl triflate, 139427-97-7; 4-methoxycubane carboxylic acid, 139427-98-8.

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(14) Admittedly in a somewhat different solvent system.

(15) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.*, in press.

Double Cycloaromatization of (*Z*,*Z*)-Deca-3,7-diene-1,5,9-triyne: Evidence for the Intermediacy and Diradical Character of 2,6-Didehydronaphthalene

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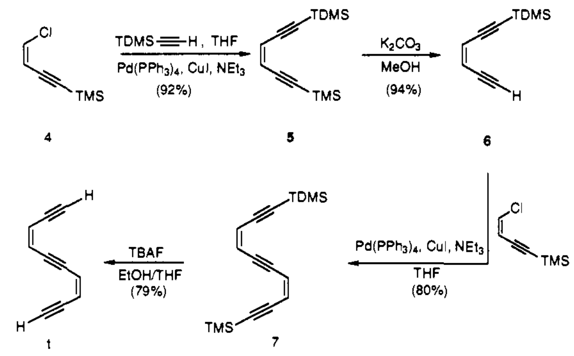
The thermal cycloaromatization reactions of hex-3-ene-1,5-diynes to form 1,4-didehydrobenzene intermediates were first studied in our laboratories several years ago.[1-4] Such intermediates are now thought to play a critical role in the DNA-cleaving activity of an emerging class of powerful antitumor antibiotics. The isolation of natural products such as the esperamicins, calicheamicins, and dynemicins has stimulated numerous synthetic, mechanistic, and biological activity studies.[5,6] The renaissance of research in this area has prompted us to return to the chemistry of a variety of substituted enediyne systems in the hope of discovering new types of dehydroaromatic biradical intermediates. Our first goal was the synthesis and thermal reactions of the extended enediyne system (*Z*,*Z*)-deca-3,7-diene-1,5,9-triyne (**1**). We present experimental evidence that heating **1** leads to 2,6-didehydronaphthalene.[7,8]

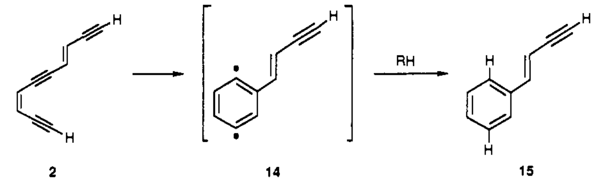
The stereospecific synthesis of the requisite dienetriynes utilized standard nickel-[9] and palladium-catalyzed[10,11] coupling methodology. The synthesis of the *Z*,*Z* isomer is outlined in Scheme I; the *E*,*Z* and *E*,*E* isomers **2** and **3**, respectively, are prepared by analogous methods. Enyne **4**[12] was coupled with (dimethylthexylsilyl)acetylene[13-15] to afford enediyne **5**. Selective removal of the trimethylsilyl group[13] of **5** was cleanly achieved with potassium carbonate in methanol to afford **6**, which could be subsequently coupled with (*Z*)-vinyl chloride **4** to afford the fully protected extended system **7**. Compound **7** is a stable oil and can be stored indefinitely at room temperature in the dark. Both of the silyl protecting groups of **7** could be cleanly removed with tetrabutylammonium fluoride in ethanol/THF to afford **1** in good yield after chromatographic purification. The unprotected dienetriynes readily polymerize when neat; however, they may be stored indefinitely in solution (0.01 M) at −60 °C.

Scheme I



[TDMS = $(CH_3)_2SiC(CH_3)_2CH(CH_3)_2$; TMS = $(CH_3)_3Si$]

Scheme II



Thermolysis of dilute solutions of **1** (<0.005 M, 170–190 °C) in a variety of solvents resulted in double cycloaromatization to give naphthalene. Despite extensive efforts, we have been unable to increase the yields of naphthalene above about 10%. However, all mechanistic and tracer experiments carried out on this thermolysis are consistent with the formation of didehydronaphthalene diradical **9** (Scheme III). The disappearance of **1** is first-order and proceeds with a rate constant of $6.2 \times 10^{-3}\ s^{-1}$ (0.004 M, acetone, 190 °C).[16] Thermolysis in acetone-d_6 led to the formation of naphthalene-d_2 containing deuterium atoms exclusively in the β-positions (>95% by ^2H NMR spectrometry). The naphthalene-d_2 was isolated by preparative GC and shown to have ^1H and ^{13}C NMR spectra identical to those of an authentic sample of naphthalene-*2,6*-d_2 synthesized by the treatment of 2,6-dibromonaphthalene[17] with 5 equiv of *n*-butyllithium (THF, −78 °C) followed by quenching with D_2O. Thermolysis of **1** in acetone led to only one other major product (ca. 5%) detectable by GC: ketone **11** (isolated by preparative GC), uncontaminated with its α-isomer.[18] We believe this material is also derived from diradical

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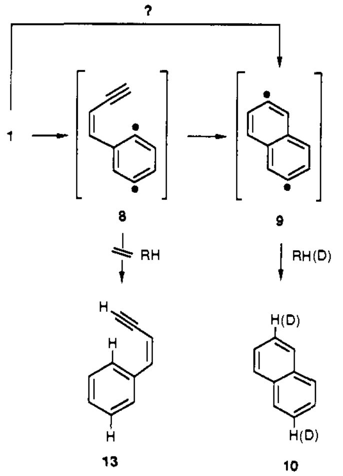
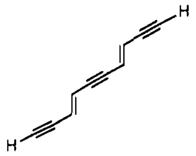
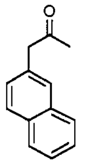
Scheme III



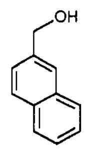
9 by hydrogen atom transfer from the acetone followed by combination of the resulting 2-naphthyl and α-acetonyl radicals. Similarly, thermolysis of **1** in methanol led to the formation of 2-naphthalenemethanol (**12**) uncontaminated with 1-naphthalenemethanol.



3



11



12

The thermolyses of *E,Z* and *E,E* dienetriynes **2** and **3** contrasted sharply with the behavior of *Z,Z* isomer **1**. No naphthalene was detected by GC in either of these reactions. Thermolysis of **2** (Scheme II) in dilute solution at 170–190 °C gave cyclized product **15**[19] (ca. 20%), in analogy to the reactivity seen for simple enediyne systems.[1-4] *E,E* isomer **3** is more stable at 170–190 °C, undergoing only slow disappearance (presumably polymerization). Heating **13**,[19] the cis isomer of **15** and potential monocyclization product of **1**, under conditions similar to those used in the thermolysis of **1** demonstrated that **13** decomposes slowly but does not form naphthalene.[20]

These data suggest that the naphthalene formed from **1** arises from 2,6-didehydronaphthalene and that this reactive intermediate has a diradical structure analogous to that of 1,4-didehydrobenzene.[1-4] Benson group equivalent calculations[21] suggest that diradical **8** has an enthalpy of formation approximately 10 kcal/mol higher than dienetriyne **1**, but that diradical **9** has an enthalpy of formation approximately *50 kcal/mol lower* than that of **1**.[22] It is of interest that monocyclized diradical **14** can be trapped to give **15** in the thermolysis of **2**, but no **13** is observed in the thermolysis of **1**. This suggests that either the 1,4-didehydrobenzene intermediate **8** cyclizes very rapidly to **9** or the cyclization of **1** to **9** is a concerted process. The cyclization of the 1,3-hexadien-5-ynyl radical to phenyl radical, analogous to the transformation of **8** to **9**, is thought to be a facile process.[23,24]

The double cycloaromatization of **1** demonstrates that arene diradicals larger than 1,4-didehydrobenzene may be accessible through appropriate poly-enyne cyclizations. This has the potential of increasing our fundamental knowledge of these unique intermediates and of widening the range of calicheamicin-type DNA-cleaving reagents to systems that have not previously been available. Further studies on systems related to **8** and **9** are in progress.

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Supplementary Material Available: Listings of IR, MS, ^1H NMR, ^{13}C NMR spectral data of all new compounds mentioned in the text, a general description of the kinetics experiments, and plots of rate data (9 pages). Ordering information is given on any current masthead page.

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A New Family of 14-Vertex Hexacapped Metal Cubes with Main Group IV (14) Atoms: Synthesis and Structural-Bonding Analysis of $Ni_9(\mu_4\text{-}GeEt)_6(CO)_8$ Containing a Nickel-Centered $Ni_8(\mu_4\text{-}Ge)_6$ Cubic Cage with an Unusual Electron Count

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Our efforts to incorporate main-group elements into transition metal clusters have recently focused on group IV (14) reagents. Reactions of $RSnCl_3$ (R = Me, *n*-Bu) with $[Ni_6(CO)_{12}]^{2-}$ (**1**)[2] gave rise to a new family of icosahedral cages with main group 14 atoms, viz., the 158-electron $[Ni_{11}(SnR)_2(CO)_{18}]^{2-}$ dianions (R = Me, *n*-Bu) with Ni-centered 1,12-$Ni_{10}Sn_2$ icosahedral cages as well as their $[Ni(SnRCl_2)_4(CO)]^{2-}$ precursors with trigonal-bipyramidal d^8 Ni(II) configurations.[3]

We report herein that a similar reaction of **1** with another main group 14 organotrihalide, $EtGeCl_3$, has produced the neutral $Ni_9(\mu_4\text{-}GeEt)_6(CO)_8$ (**2**) with a nickel-centered Ni_8 cube capped on all six faces by germylidene ligands.[4,5] Other clusters with noncentered and metal-centered $M_8(\mu_4\text{-}E)_6$ cubic cages are known

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(1) (a) University of Wisconsin–Madison. (b) Current address: Argonne National Laboratory, Chemical Technology Division, 9700 South Cass Avenue, Argonne, IL 60439. (c) Science Institute, University of Iceland.

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