downfield shift. The former resonance is assigned to the selenonium cation and the latter peak to the selenurane structure;[11] particularly, each peak exhibits two clearly resolved satellite peaks due to the ^{77}Se–^{77}Se coupling (large coupling constant of $^1J_{Se-Se}$ = 210 Hz) about each central peak.[12] This observation of ^{77}Se satellites clearly indicates the occurrence of bond formation between the three selenium atoms.

A new selenurane $2PF_6^-$ salt **2a** (mp 190 °C, dec) was isolated in the two-electron oxidation of **1** with 2 equiv of $NOPF_6$, a one-electron oxidant, in CH_3CN.[13] The selenurane **2a** was stable and easily handled. The structure of **2a** in CH_3CN was analyzed by multinuclear NMR spectroscopy.[5] Specifically, the ^{77}Se NMR spectrum of **2a** shows two resonances at δ 535.2 ($SeCH_2Ar$) and δ 830.0 (SeAr), and the ^{77}Se satellites in the proton-decoupled ^{77}Se NMR spectrum of **2a** give a value of 200 Hz for $^1J_{Se-Se}$; i.e., **2a** has the selenurane structure having two apical selenonium cations. The selenurane **2a** exists solely as a single conformer from −40 to +75 °C as evidenced by its ^1H NMR spectrum. The conformation of **2a** was fixed as the boat form by transannular bonds between the three selenium atoms, although normally the chair conformer has been shown to be more stable and rigid than the boat conformer.[6]

Analogously, oxidation of **3** with concentrated H_2SO_4 or 2 equiv of $NOPF_6$ gave the selenurane **4** or its salt **4a** (mp 185 °C, dec).[5] The ^{77}Se NMR spectrum of **3** in $CHCl_3$ shows a singlet peak at δ 207.0, while **4a** in CH_3CN shows a singlet at δ 946.7, as is characteristic of a selenurane.[11] This is the first example of multicentered bond formation involving two different chalcogens.

The redox behavior of **2a** was examined since little information on the reactivity of selenuranes was available.[3] Treatment of benzenethiol (PhSH) (2 equiv) with **2a** (1 equiv) in CH_3CN under an Ar atmosphere at room temperature for 1 h gave diphenyl disulfide (PhSSPh) (87%) as the oxidation product and neutral **1** (85%) as the reduction product. Similar reaction of **2a** with triphenylphosphine (Ph_3P, 2 equiv) afforded **1** (90%) and the phosphine oxide ($Ph_3P{=}O$) (76%) after treatment with H_2O.[14] The selenurane **2a** could also be reduced by phenothiazine (**5**, 2 equiv) in CH_3CN to give **1** (91%) by two-electron transfer, accompanied by the formation of the cation radical of **5** as evidenced by the UV-visible spectrum (λ_{max} = 437 and 515 nm).[15] Interestingly, **2a** undergoes two-electron reduction to give **1** in quantitative yield by treatment with samarium(II) iodide, SmI_2,[16] at room temperature. From these novel results, an electron-transfer pathway is likely and **2a** is a good oxidant.

Reduction of **2a** is also facile electrochemically; cyclic voltammetry of **2a** in CH_3CN reveals that the reduction potential is remarkably lower (−0.10 V vs Ag/0.01 M $AgNO_3$) than those of some selenonium salts (ca. −1.5 to −1.8 V vs Ag/0.01 M $AgNO_3$)[17] and ammonioselenuranes[1c] (−0.8 to −2.0 V vs Ag/0.01 M $AgNO_3$),[17] though the electrochemistry of selenuranes and selenonium salts is virtually unknown.

Thus, the facile structural changes (chair $\rightleftharpoons$ boat) in the redox reactions of **1** or **3** are ascribed to the stabilization of the oxidized species by multicenter chalcogenide participation, i.e., the formation of selenurane dications, and the destabilization by transannular lone pair–lone pair repulsion of the neutral boat forms derived from the reduction of the dications. Further studies on the structural changes during electrochemical oxidation and reduction of the tris-chalcogenides are in progress.

Acknowledgment. This work was supported by a grant-in-aid for Scientific Research on a Priority Area of Organic of Unusual Valency (No. 03233101) from the Ministry of Education, Science and Culture, Japan. One of us (H.F.) acknowledges a Scientific Research grant (No. 03640435) from the Ministry of Education, Science and Culture, Japan.

Registry No. 1, 139526-19-5; **2**, 139526-21-9; **2a**, 139526-25-3; **3**, 139526-22-0; **4**, 139526-24-2; **4a**, 139526-26-4; ^{77}Se, 14681-72-2.

Supplementary Material Available: Proton-noise-decoupled ^{77}Se NMR spectrum of selenurane **2a** (2 pages). Ordering information is given on any current masthead page.

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[11] Generally, the ^{77}Se chemical shifts of selenonium compounds are δ 300–600, while those of selenuranes are δ 400–1100.[12]

[12] Chapter 6 of ref 3a. Reference 3b. Iwamura, H.; Nakanishi, W. *Yuki Gosei Kagaku Kyokaishi (Japan)* **1981**, *39*, 795–804.

[13] **2a**: Anal. Calcd for $C_{16}H_{14}Se_3P_2F_{12}$: C, 26.21; H, 1.92. Found: C, 26.39; H, 1.82. Although **2a** has been obtained in solid form, we have as yet been unable to grow crystals suitable for X-ray analysis.

[14] Ph_3P is known to transfer an electron to a suitable acceptor, resulting in the formation of its phosphinium cation radical which reacts with H_2O to give $Ph_3P{=}O$; Powell, R. L.; Hall, C. D. *J. Am. Chem. Soc.* **1969**, *91*, 5403–5404.

[15] Bodea, C.; Silberg, I. *Adv. Heterocycl. Chem.* **1968**, *9*, 321–460.

[16] (a) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698. (b) Soderquist, J. A. *Aldrichimica Acta* **1991**, *24*, 15–23.

[17] Fujihara, H.; Furukawa, N. Unpublished results.

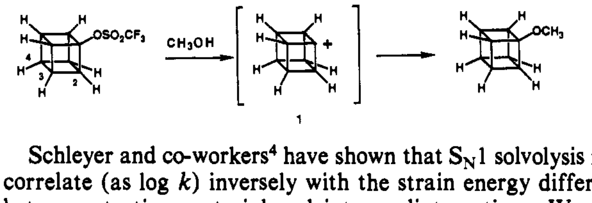
On the Nature of Cubyl Cation

Philip E. Eaton* and Jian Ping Zhou

Department of Chemistry, The University of Chicago
5735 South Ellis Avenue, Chicago, Illinois 60637

Received January 6, 1992

Cubanes carrying good nucleofugal substituents undergo remarkably rapid solvolysis.[1,2] For example, the half-life of cubyl triflate in methanol is 15 min at 70 °C. The reaction (eq 1) is clean and proceeds without rearrangement; cubyl methyl ether is formed in high yield. Sufficient data has been presented already to establish that such reactions proceed by way of cubyl cation (**1**).[1-3]



(1)

Schleyer and co-workers[4] have shown that S_N1 solvolysis rates correlate (as log *k*) inversely with the strain energy difference between starting material and intermediate cation. We have constructed Table I by taking published rate data for solvolysis, "correcting" it insofar as possible to a common set of conditions,[5] and comparing the results to the predictions of molecular mechanics.[4] Within 1 or 2 powers of ten, the agreement is excellent except for the cubane system. In this case, theory and experiment differ by more than 15 powers of ten!

What is so different about the cubane system? Borden and Hrovat have applied ab initio 6-31G* calculations (including electron correlation) to cubyl cation and have concluded that delocalization of the positive charge occurs via interaction with the strained, p-rich cubane CC bonds.[6] No comparable interaction is found by calculation in the cation from any other system in Table I. In the cubyl case there is a positive bond order between the p orbital at the cation carbon and the p orbital aligned with it at each of the β carbons (C-3). Population analysis reveals that the γ-CH (C-4) and α-CH (C-2) groups bear considerable positive charge (0.16) and more than the β-CH groups. As such delocalization of charge is not considered in classical molecular mechanics calculations, it is no wonder that the deviation boxed in Table I is so large.

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[1] Eaton, P. E.; Yang, C.-X.; Xiong, Y. *J. Am. Chem. Soc.* **1990**, *112*, 3225.

[2] Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, A. K. *J. Am. Chem. Soc.* **1990**, *112*, 3228.

[3] Kevill, D. N.; D'Souza, M. J.; Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, A. K. *J. Chem. Soc., Chem. Commun.* **1990**, 623.

[4] (a) Gleicher, G. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 582. (b) Bingham, R. C.; Schleyer, P. v. R. *Ibid.* **1971**, *93*, 3189. (c) Sherrod, S. A.; Bergman, R. G.; Gleicher, G. J.; Morris, D. G. *Ibid.* **1972**, *94*, 4615. (d) For important extensions, see: Müller, P.; Mareda, J. *Helv. Chim. Acta* **1987**, *70*, 1017. (e) **Note Added in Proof.** For a newer molecular mechanics treatment of the cubyl cation done ex post facto its unexpected ease of generation, see: Müller, P.; Milin, D. *Helv. Chim. Acta* **1991**, *74*, 1808.

[5] (a) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846. (b) Bentley, T. W.; Roberts, K. *J. Org. Chem.* **1985**, *50*, 4821.

[6] Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 3227.

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Table I. Experimentally- and Calculationally-Derived Relative Solvolysis Rates of Some Tertiary Tosylates in Acetic Acid at 70 °C

tosylate	found	predicted
tert-butyl[a]	1	1
1-adamantyl[b]	10^{-3}	10^{-4}
1-bicyclo[2.2.2]octyl[b]	10^{-7}	10^{-8}
1-norbornyl[b]	10^{-13}	10^{-14}
cubyl[c]	10^{-10}	$<10^{-25}$

[a] References 5a and 4b. [b] Reference 4b. [c] References 1, 5b, and footnote 73 in 4b.

Table II. Pseudo-First-Order Rate Constants for the Solvolysis of Various 4-X-1-Y-Cubanes

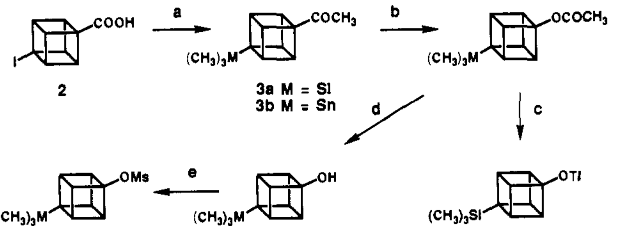
X	Y	temp, °C	solvent	rate constant k, 10^{-6} s^{-1}
H	OTf	25.0	CH_3OH	2.9[a]
H	OTf	50.1	CH_3OH	77.2
CH_3	OTf	50.0	CH_3OH	41
Cl	OTf	60.0	$(CF_3)_2CHOH$	0.32
OCH_3	OTf	60.0	$(CF_3)_2CHOH$	1.45
$Si(CH_3)_3$	OTf	25.0	CH_3OH	316
$Si(CH_3)_3$	OMs	30.0	$(CF_3)_2CHOH$	42.4
$Si(CH_3)_3$	OMs	40.0	$(CF_3)_2CHOH$	111
$Si(CH_3)_3$	OMs	50.0	$(CF_3)_2CHOH$	253
$Si(CH_3)_3$	OMs	15.0	$(CF_3)_2CHOH$	9.6[a]
$Sn(CH_3)_3$	OMs	15.0	$(CF_3)_2CHOH$	246
$Sn(CH_3)_3$	OMs	50.0	CF_3CH_2OH	48.8

[a] Extrapolated.

In effect, the ab initio calculations define cubyl cation as a nonclassical ion. This view has been challenged by Kevill and Moriarty et al.[2,3] on the idea that the effects of substituents at the 4 position on the rate of cubyl triflate solvolysis are not accommodated by this description. Electron-withdrawing substituents all depress the rate of solvolysis tremendously (as would happen with any picture of the cation) but, they stress, the rate reductions are fairly insensitive to substituent. There is no correlation with Brown σ_p^+ constants "as one would expect" if there were substantial charge delocalization to the 4 position. Similarly, the fact that a methyl group at position 4 depresses the rate of solvolysis is taken as evidence against charge delocalization to this position.[7]

We have no quarrel with the data of Kevill and Moriarty.[2,3] Our own results are similar and are reported along with some important new data in Table II.[1] But to our way of thinking, the effects of substituents are exactly in accord with expectation. Borden has insightfully pointed out that the LUMO of the delocalized cubyl cation is cylindrically symmetric along the body diagonal of the cube. Therefore, electron donation from substituent orbitals off this axis will be ineffective.[6] The rate reductions should not follow Brown σ_p^+ constants but should be roughly in accord with Charton σ_I or Grob σ_I^q inductive constants,[8,9] just as Kevill and Moriarty have, in fact, found. The usual amelioration of inductive electron-withdrawal by resonance effects so typical for halogen substituents is much reduced as a consequence of the symmetry constraint. Similarly, we have found that it is the destabilizing, inductive electron-withdrawing effect of the methoxy group, rather than its usual and powerful cation-stabilizing resonance effect, that is important in the cubane case; the solvolysis of 4-methoxycubyl triflate[10] is exceedingly slow (Table II). For the same reason, hyperconjugative stabilization by a methyl group at position 4 is rendered ineffective by the off-axis positioning of the methyl C–H bonds relative to the symmetry axis of the cation LUMO.[1,6] Only the geometry-independent, electron-withdrawing inductive effect of the methyl group remains significant.[7]

Scheme I[a]



[a] (a) MeMgBr/room temperature/24 h in THF/Et_2O then at −78 °C *t*-BuLi followed by TMSnCl (**3b**, 71%). (b) *m*-ClPhCOOOH/room temperature/17 h in CH_2Cl_2 (M = Si, 98%, mp 23–25 °C; M = Sn, 71%, mp 40–42 °C). (c) DIBAH/−70 °C/2 h in toluene then Tf_2O and warmed to room temperature (**4**, 58%, mp 42–43 °C). (d) DIBAH/−70 °C/2 h in toluene then water (used crude). (e) $MeSO_2Cl/Et_3N$/−20 °C/30 min in CH_2Cl_2 (**5a**, 80%, mp 85–86 °C; **5b**, 67%, mp 76–78 °C).

Orbital alignment is important for π-donation, but it has no bearing on σ-donation. If therefore, as we propose, there is charge delocalization to the 4 position of cubyl cation, groups capable of σ-donation should stabilize the cation and enhance the rate of solvolysis of its parent. Now, we show this to be the case.

Methyl 4-(trimethylstannyl)cubyl ketone (**3a**) was prepared as shown in Scheme I from 4-iodocubanecarboxylic acid (**2**).[11] The corresponding 4-trimethylsilyl compound **3b** was obtained by a related set of conversions. Baeyer–Villiger oxidation of each methyl ketone to the corresponding acetate proceeds readily at room temperature; in the tin case, the reaction must be monitored (TLC) as an overly long reaction time leads to oxidative cleavage of the tin moiety. 4-(Trimethylsilyl)cubyl triflate (**4**) was obtained by quenching the DIBAH reduction of the acetate directly with triflic anhydride. The tin analogue was too unstable to isolate.

The solvolysis of 4-(trimethylsilyl)cubyl triflate in methanol at 25.0 °C was followed by calibrated GLC. The reaction is clean, pseudo-first-order over at least 3 half-lives, and produces only (4-trimethylsilyl)cubyl methyl ether. The rate constant is about 110 times greater than that of cubyl triflate. The enhanced rate is in accord with expectation for a substituent whose electron donation is unimpeded by symmetry considerations.

As 4-(trimethylstannyl)cubyl triflate could not be isolated, the solvolyses of the 4-trimethylsilyl (**5a**) and 4-trimethylstannyl (**5b**) mesylates (Scheme I) were compared instead. The reactions in methanol are too slow to follow conveniently. The more ionizing hexafluoroisopropyl alcohol gives clean, pseudo-first-order reactions, producing only the corresponding cubyl hexafluoroisopropyl ethers. The rate constant for **5a** was determined at 30.0, 40.0, and 50.0 °C ($E_{act.}$ = 17.4 kcal/mol) and extrapolated to 15.0 °C where it was possible to measure the rate for **5b**.[12] 4-(Trimethylstannyl)cubyl mesylate is solvolyzed about 26 times faster than its silyl analogue. If we correct (insofar as possible) for solvent, temperature, and leaving group, we deduce that 4-(trimethylstannyl)cubyl triflate would undergo solvolysis over 2800 times faster than cubyl triflate itself!

Moriarty has attributed the effect of substituents on cubyl triflate solvolysis rate to "... a highly effective transannular transmission of the polar effect ...".[2] However, polar field effects in the solvolysis of 3-X-adamantyl halides give rise to rate enhancements of no more than 8.6 and 58 for X = trimethylsilyl and trimethylstannyl, respectively,[13] far less than the factors of

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[7] Note, however, that a methyl group at position 2 does accelerate the solvolysis: $k = 2.4 \times 10^{-4}$ s^{-1} at 50 °C in methanol.[1]

[8] Charton, M. *J. Org. Chem.* **1964**, *29*, 1222.

[9] Grob, C. A.; Schaub, B.; Schlageter, N. G. *Helv. Chim. Acta* **1980**, *63*, 57.

[10] 4-Methoxycubanecarboxylic acid was prepared by photolysis of the iodo acid in methanol (cf. Reddy, D. S.; Sollott, G. P.; Eaton, P. E. *J. Org. Chem.* **1989**, *54*, 722) and converted to 4-methoxycubyl triflate by reactions like those in Scheme I.

[11] Tsanaktsidis, J.; Eaton, P. E. *Tetrahedron Lett.* **1989**, *30*, 6967.

[12] It was necessary to add 1 equiv of triethylamine to suppress protonolysis of the cubyl tin bond by methanesulfonic acid generated during the solvolysis.

[13] See the references and fine discussion in the following: Adcock, W.; Krstic, A. R.; Duggan, P. J.; Shiner, V. J., Jr.; Coope, J.; Ensinger, M. W. *J. Am. Chem. Soc.* **1990**, *112*, 3140. See also: Adcock, W.; Coope, J.; Shiner, V. J., Jr.; Trout, N. A. *J. Org. Chem.* **1990**, *55*, 1411.

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

Kamal N. Bharucha, Rebecca M. Marsh, Robert E. Minto, and Robert G. Bergman*

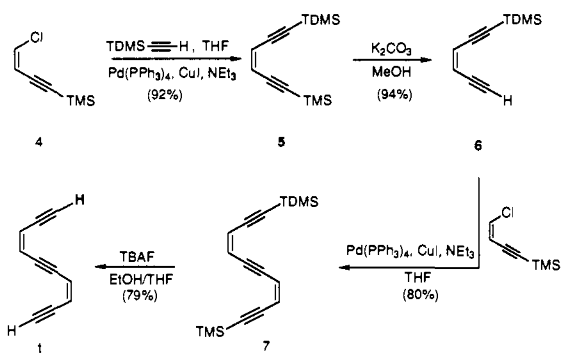
Department of Chemistry, University of California
Berkeley, California 94720

Received December 11, 1991

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]

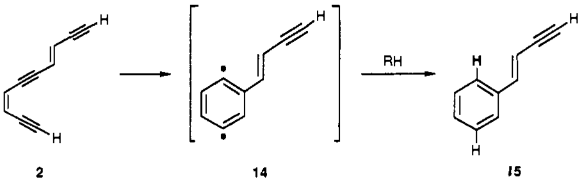
The stereospecific synthesis of the requisite dienetriynes utilized standard nickel-[9] and palladium-catalyzed[10,11] coupling methodology. The synthesis of the *Z*,*Z* isomer is outlined in Scheme I; the *E*,*Z* and *E*,*E* isomers **2** and **3**, respectively, are prepared by analogous methods. Enyne **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 ^{2}H NMR spectrometry). The naphthalene-d_2 was isolated by preparative GC and shown to have ^{1}H 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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(1) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25.

(2) Lockhart, T. P.; Comita, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *102*, 4082.

(3) Lockhart, T. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4090.

(4) Jones, R. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660.

(5) Nicolaou, K. C.; Dai, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387.

(6) (a) Lee, M. D.; Ellestad, G. A.; Borders, D. B. *Acc. Chem. Res.* **1991**, *24*, 235. (b) Lee, M. D.; Dunne, T. S.; Chang, C. C.; Siegel, M. M.; Morton, G. O.; Ellestad, G. A.; McGahren, W. J.; Borders, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 985 and references cited therein.

(7) Detection of a number of isomeric dehydronaphthalenes, including 2,6-didehydronaphthalene, by pyrolysis–mass spectrometry has been reported. See: Grützmacher, H. F.; Lehmann, W. R. *Liebigs Ann. Chem.* **1975**, 2023.

(8) For an extended Hückel treatment of dehydroaromatics, including 2,6-didehydronaphthalene, see: Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.

(9) For the application of nickel-catalyzed coupling methodology to the synthesis of all-trans oligomeric enyne systems, see: Wudl, F.; Bitler, S. P. *J. Am. Chem. Soc.* **1986**, *108*, 4685.

(10) Alami, M.; Linstrumelle, G. *Tetrahedron Lett.* **1991**, *32*, 6109.

(11) Vollhardt, K. P. C.; Winn, L. S. *Tetrahedron Lett.* **1985**, *26*, 709.

(12) Kende, A. S.; Smith, C. A. *Tetrahedron Lett.* **1988**, *29*, 4217.

(13) (a) Radde, R. Ph.D. Thesis, University of California, Berkeley, CA, 1989. (b) Stracker, E. C.; Zweifel, G. *Tetrahedron Lett.* **1991**, *32*, 3329. For another synthesis of **6**, see: (c) Porco, J. A., Jr.; Schoenen, F. J.; Stout, T. J.; Clardy, J.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 7410.

(14) Midland, M. M. *J. Org. Chem.* **1975**, *40*, 2250.

(15) Wetter, H.; Örtle, K. *Tetrahedron Lett.* **1985**, *26*, 5515.

(16) The rate of appearance of naphthalene was also first-order, with $k = 4 \times 10^{-3}\ s^{-1}$.

(17) Blatter, K.; Schlüter, A. D. *Synthesis* **1989**, 356.

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