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Thermal Cyclization of 1-{(Z)-1-Hexene-3,5-diynyl}-2-(1,3-butanediynyl)benzene Leading to Dinaphtho[1,2-*b*:2,1-*f*]semibullvalene and Dinaphtho[2,1-*b*:1,2-*j*]elassovalene Skeletons via Cyclobuta[*a*]naphthalene

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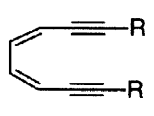
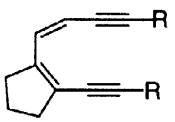
Abstract: Conjugated aromatic diene-diyne (**3**) undergoes thermal cyclization at 80 °C to form cyclobuta[*a*]naphthalene (**4**), leading to polycyclic compounds, dinaphtho[1,2-*b*:2,1-*f*]semibullvalene (**5**) and dinaphtho[2,1-*b*:1,2-*j*]elassovalene (**7**).

Thermal radical cycloaromatization reactions of enyne derivatives have attracted much attention for the preparation of polycyclic ring systems in recent years.[1] An intramolecular [2+2]cycloaddition of (*Z,Z*)-3,5-octadiene-1,7-diynes (**1** and **2**) to benzocyclobutadienes has been reported.[2,3] To our knowledge, the [2+2] cycloaddition of aromatic diene-diynes (**3**) remains to be investigated. Herein, we report the synthesis and isolation of dinaphtho[1,2-*b*:2,1-*f*]semibullvalene (**5**) and dinaphtho[2,1-*b*:1,2-*j*]elassovalene (**7**) which are formed by radical cyclization of **3**, followed by valence isomerization in a nitrogen stream at 80 °C in the dark. Compound **6** (not isolated) is of interest due to its possible high degree of strain and potential use as a precursor of elassovalene systems (e.g., **7**). Additionally, a postulated biradical intermediate (**14**) may serve as a DNA-cleaving reagent.[4] The facility of the **3** → (**5** and **7**) conversion prompts us to communicate our preliminary observations at this time.



1



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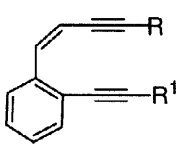
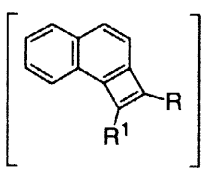
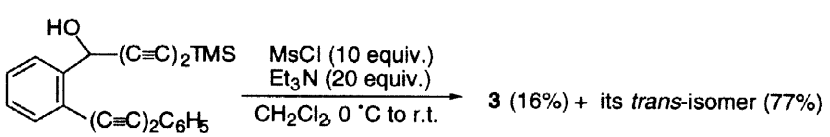


3: R=C≡CTMS, R^1=C≡CC_6H_5



4:R=C≡CTMS, R^1=C≡CC_6H_5

Compound **3** was prepared as follows:



Thermolysis of **3** (5 mM) in benzene in the presence of 10 equivalents of 1,4-cyclohexadiene at 80 °C for 22 h in the dark yielded two components of **5**[1] (colorless columns; 42%) and **7** (yellow columns; 18%) after

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purification by silica gel chromatography (eluent; benzene and hexane) and recrystallization from dichloromethane and hexane. Thus, compound **5** was isolated as stable crystals. The crystals of **7** which contained a hexane molecule in a (1 : 1) ratio to **7**, were shown to be stable only in a hexane solution or in a sealed tube under hexane atmosphere. Being allowed to stand in air, these crystals gradually changed to amorphous powders. The corresponding elassovalene derivative which may be formed by thermal cyclization of **5** was not established in the reaction mixture obtained from this reaction. The physicochemical properties and spectral data of both compounds are given in Table 1.

Scheme 1.

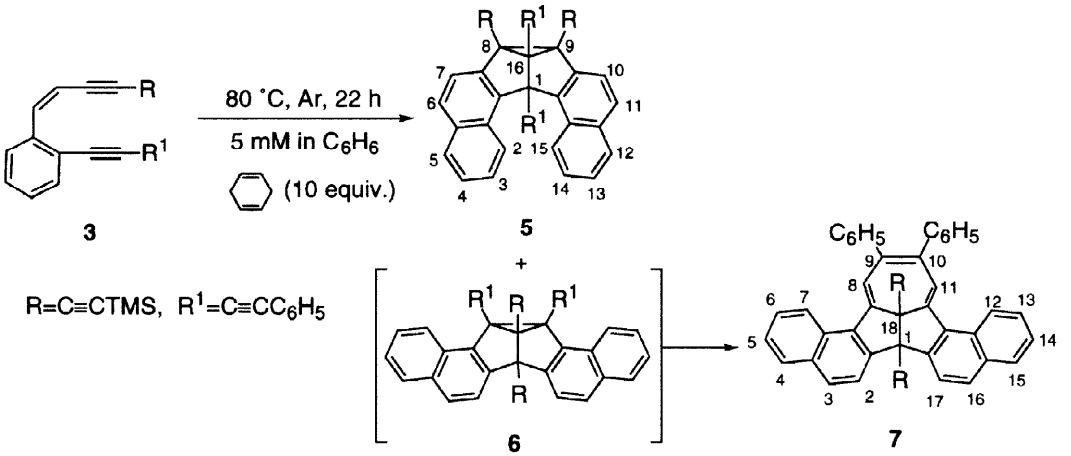


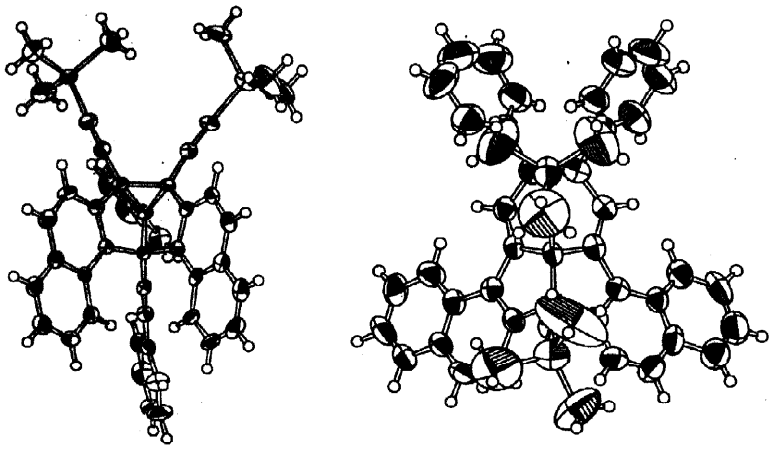
Table 1. Physicochemical Properties and Spectral Data of **5** and **7**

	5	**7**[a]
Crystal form	colorless columns (CH_2Cl_2-hexane)	yellow columns (CH_2Cl_2-hexane)
Molecular Formula	$C_{50}H_{40}Si_2$	$C_{50}H_{42}Si_2$
Mp	231 °C (dec.)	290 °C (dec.)
IR (KBr) ν	2180 cm^{-1}	2166 cm^{-1}
UV (CH_3CN), λ (log ε)	249 (4.8), 258 (4.8) nm	338 (4.6), 253 (4.7) nm
^{1}H-NMR (400 MHz, $CDCl_3$) δ	9.44 (d, 2H, *J*=8.5 Hz), 7.69-7.59 (m, 8H) 7.52-7.48 (m, 2H), 7.41-7.32 (m, 6H), 7.27-7.20 (m, 6H), 0.283 (s, 18H)	8.45 (d, 2H, *J*=8.3 Hz), 8.08 (d, 2H, *J*=8.6 Hz), 7.90 (d, 2H, *J*=8.6 Hz), 7.84 (d, 2H, *J*=7.1 Hz), 7.78 (s, 2H), 7.53-7.49 (t-like, 2H), 7.46-7.42 (t-like, 2H), 7.37-7.35 (d-like, 4H), 7.26-7.17 (m, 6H), 0.26 (s, 9H), 0.07 (s, 9H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ	143.7, 133.9, 131.8, 131.7, 131.1, 129.3, 128.5, 128.4, 128.0, 128.0, 127.7, 126.1 125.4, 123.4, 123.1, 100.4, 93.1, 92.1, 89.8, 87.7, 81.7, 61.2, 53.8, 30.9, 0.223.	146.7, 143.5, 140.8, 135.9, 134.2, 131.2, 130.3, 130.2, 129.4, 129.2, 127.6, 126.2 125.9, 124.7, 122.4, 106.7, 102.9, 91.1, 87.8, 61.6, 57.9.
FABMS m/z	696 (M^+), 697 $(M+H)^+$	698 (M^+), 699 $(M+H)^+$
Elementary analysis Found (Calcd)	C, 85.88; H, 5.51 (C, 86.15; H, 5.79)	C, 86.10; H, 5.86 (C, 85.90; H, 6.06)

a) The physicochemical properties and spectral data of **7** were obtained from the amorphous powders

Although it was considerably difficult to determine the structure of **5** and **7** on the basis of spectral data and elementary analyses, finally, their structure was confirmed by an X-ray crystal analysis of **5** and **7**. The ORTEP structures of **5** and **7** are shown in Figure 1.[2] Compound **5** was shown to have a semibullvalene skeleton bearing vicinal trimethylsilylethynyl groups at the C-8 and C-9 positions with good symmetry and two phenylethynyl groups at the C-1 and C-16 positions. On the other hand, **7** was shown to have an elassovalene skeleton bearing two trimethylsilylethynyl groups at the C-1 and C-18 positions, which groups were indicated to

be nonequivalent from the signal of trimethylsilyl groups in the ^{1}H-NMR spectrum.



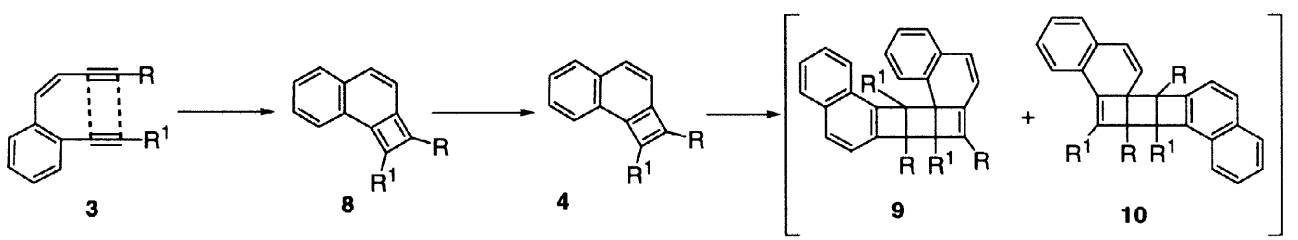
5 7

Figure 1. The ORTEP drawings of **5** and **7**

In order to obtain insight into the mechanism of the thermal cyclization, the reaction of **3** in benzene was carried out in the presence of 2-propanol-d_8 as cosolvent (10 %; v/v) under almost the same conditions as described above to yield **7**-d_2 deuterated at the C-8 and C-11 positions, indicating that a biradical intermediate (**14**) was to be the putative radical intermediate, along with **5** (>50% by ^{2}H-NMR spectrometry).

The formation of **7** was particularly unexpected. A proposed mechanism of **5** and **7** is presented in Schemes 2 and 3. At the initial step of this reaction, the [2+2]cycloaddition reaction of **3** yields **4** via 2,3-benzobicyclo[4.2.0]octa-1(8),2,4,6-tetraene (**8**), which dimerizes readily in a Diels-Alder manner to afford dinaphtho[*bg*]cyclooctatetraenes (**11** and **12**) via **9** and **10**. Valence isomerization of **11** and **12** affords dinaphthosemibullvalenes (**5** and **6** (not isolated)). As seen in Scheme 3, **6** produced *in situ* undergoes thermal cyclization to yield a biradical intermediate (**13**) of which the valence isomerization affords an elassovalene biradical (**14**). The putative radical intermediate (**14**) was supported by deuterium incorporation at the relevant positions. The biradical **14** absorbs a hydrogen atom from the hydrogen atom donor to afford the final product **7**. The cyclization of **6** to **7** was shown to occur more readily than the conversion of 1,2-diethynylcyclopropane to a bicyclo[3,2,0]hepta-1,4,6-triene skeleton at the high temperature of 350 °C.[5]

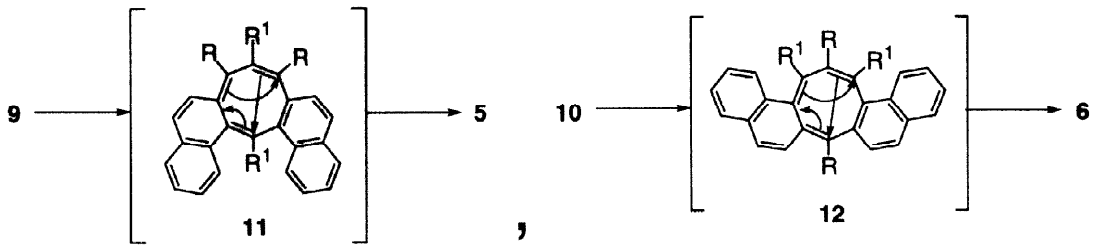
Scheme 2.



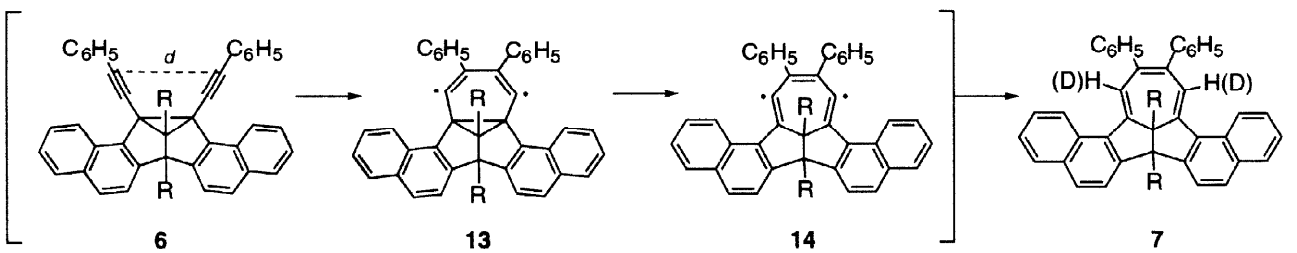
[1]All new compounds in this paper gave satisfactory IR, NMR, Mass spectra and elementary analyses. Selected physical data are given in Table 1.

[2]The crystal data for **5** (Colorless columns): Crystal dimensions=0.30x0.30x0.08 mm, Triclinic, Space group P1 (no. 2), a=14.031(2)Å, b=17.203(2)Å, c=10.643(1)Å, α=96.473(1)°, β=94.63(1)°, γ=103.826(9)°; V=2033.5 (5)Å^3, Z=2; F(000)=736; D_{calc} 1.138 g/cm^3; The final R and Rw were 0.058 and 0.062 for 3145 observed reflections (I>4.00 (σ) I). The structure of **5** was solved by direct method (SAPI91) and refined by full-matrix least-squares techniques. Diffraction data were obtained using Rigaku AFC5R diffractometer at -75 °C. The crystal data for **7** (Yellow columns): Crystal dimensions=0.30x0.15x0.10 mm, Monoclinic, Space group $P2_1/n$ (no. 14), a=9.716(3)Å, b=17.255(3)Å, c=29.137(4)Å, β=92.09(2)°; V=4881(1)Å, Z=4; F(000)=1680; D_{calc} 1.068 g/cm^3; The final R and Rw were 0.090 and 0.143 for 3002 observed reflections (I>1.50 (σ) I). The structure of **7** was solved by direct method (SHELXS86) and refined by full-matrix least-squares techniques. Diffraction data were obtained using Rigaku AFC7R diffractometer at 25 °C.

Scheme 2 (Continued).



Scheme 3.



Nicolaou has proposed that the energy of activation for the Bergman cyclization is dependent on the distance *d* of the acetylene carbons as shown in Scheme 3.[6] Snyder has proposed that the ease of cyclization of any enediyne is dependent upon the differential molecular strain between the ground state and the transition state.[7] In our case, the steric factors in the ground state that must be overcome to bring the disubstituted acetylenes close enough together to form the 1,4-biradical intermediate play an important role in determining the facility of the enediyne cyclization. The substituent on the terminal acetylene carbon, the phenyl group may decrease the energy of activation of the enediyne cyclization causing $\pi-\pi$ interaction between the phenyl groups.

In conclusion, compound **3** underwent an intramolecular [2+2]cycloaddition at 80 °C in the dark to yield cyclobuta[*a*]naphthalene (**4**). Further dimerization reaction of **4**, followed by valence isomerization afforded dinaphthosemibullvalenes (**5** and **6**). Compound **6** having vicinal phenylethynyl groups on the cyclopropane ring was shown to be converted into dinaphthoelassovalene (**7**) by the Bergman-type cyclization. Thus, thermal cyclization of **3** having a phenylethynyl substituent on the terminal acetylenic group will provide a new method for the preparation of semibullvalene and elassovalene skeletons.

Acknowledgments

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