A New Route for the Thermal Isomerization of a Highly Substituted Hexadienyne Derivative[‡]

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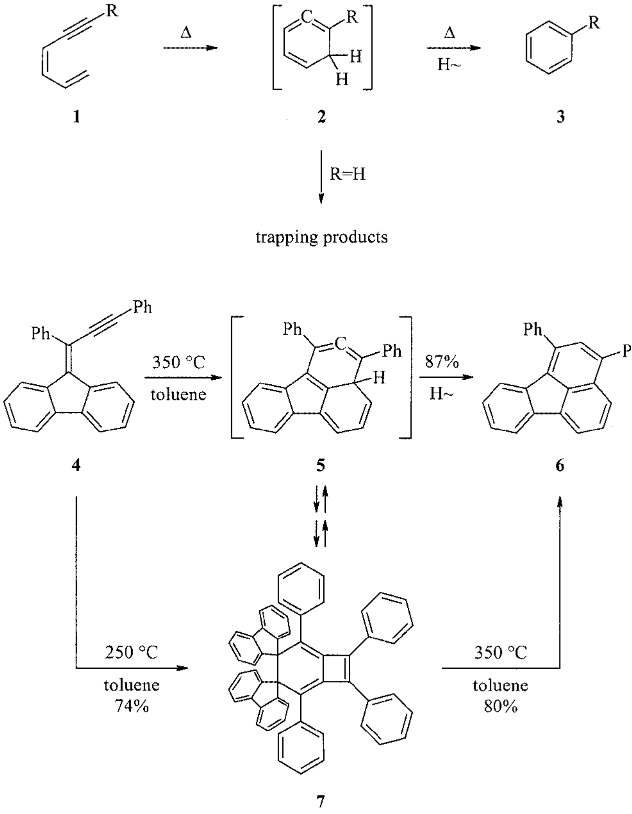
Whereas the thermal isomerization of perphenylbutenyne (**11**) at 290 °C in toluene leads to the benzannelated semibullvalene derivative **13**, pyrolysis at 360 °C furnishes the triphenylnaphthalene **12**. The mechanisms of both cycloisomerizations, which presumably proceed via the isobenzene intermediate **14**, are discussed. The structure of the rearrangement product **13** was proven by single-crystal X-ray analysis.

Introduction

On heating to about 200 °C, hexadienynes such as **1** (with R = H, D, CH_3, Br etc.), in the gas phase, cyclize in excellent yield to the corresponding benzene derivatives **3**.[2,3] As shown by trapping reactions for the parent system (R = H), the isomerization takes place in two steps proceeding via the intermediate isobenzene[4] derivative **2**.[5] In experiments using fluorene derivatives such as **4**, in which one of the double bonds of the substrate is part of a benzene ring, it was shown that at higher temperatures (350 °C, in toluene, sealed ampoule) the aromatic isomerization product, here **6**, is formed in a good yield, but that at lower temperatures (250 °C, toluene) a surprising new thermal process took place to yield the bis(methylene)cyclobutene derivative **7**. Raising the temperature to the initial value of 350 °C resulted in the cleavage of this dimer of **4** and provided the condensed aromatic hydrocarbon **6** once more (Scheme 1);[5] it is very likely that the isobenzene intermediate **5**, which in this case is also an *o*-isotoluene derivative,[6] is involved in both thermal processes. In the present communication we show that a slight modification of the substrate structure, namely the removal of the single bond connecting the two benzene rings of **4**, leads to another drastic change in mechanism, and demonstrates that the 1,3-hexadien-5-yne unit can be induced to isomerize along totally different pathways, as is the case for the even more highly unsaturated analog 3-hexen-1,5-diyne.[7,8]



Scheme 1. Thermal isomerization of hexadienynes: known cyclization routes

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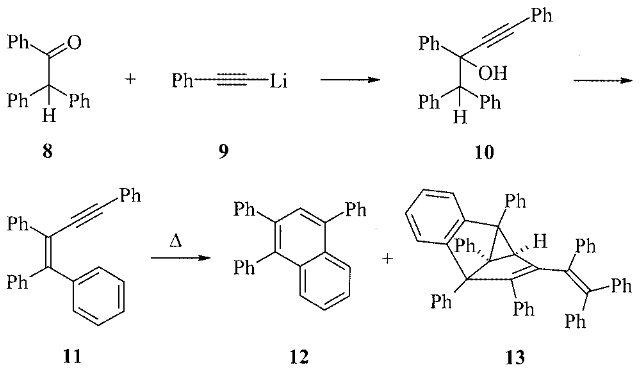
Results and Discussion

Thermal Isomerization of Perphenylbutenyne (11)

Hydrocarbon **11** was prepared according to a published procedure[9] by adding phenylethynyllithium (**9**) in a diethyl ether solution to benzhydryl phenyl ketone (**8**), and by dehydration of the thus formed propargyl alcohol **10** in toluene in the presence of potassium bisulfate at 120 °C (Scheme 2).



Scheme 2. A novel route for thermal cyclization of hexadienyne derivatives

Heating of **11** in toluene in a sealed ampoule at 360 °C for 7 h gave 1,3,4-triphenylnaphthalene (**12**) in 32% yield, a known compound[10] that was characterized by its analytical and spectroscopic data, and is the obvious result of a cycloaromatization process as discussed in Scheme 1. However, when the reaction time and temperature were lowered (290 °C, 5 h) another hydrocarbon product was isolated (31% yield), which was shown by mass spectrometry to be a dimer of the substrate **11**, but the exact structure of which could only be elucidated after single crystals suitable for an X-ray structural investigation were obtained by recrystallization from pentane. As shown in Figure 1, this novel thermal isomerization product surprisingly is a derivative of semibullvalene![11]

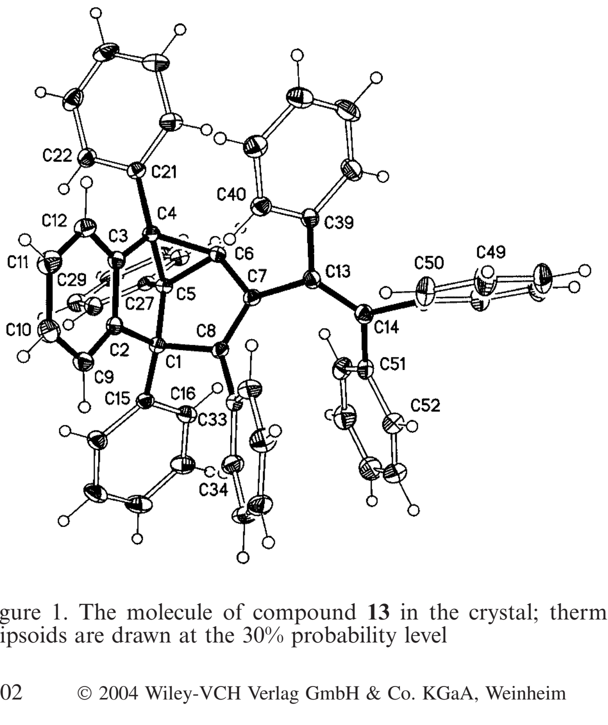
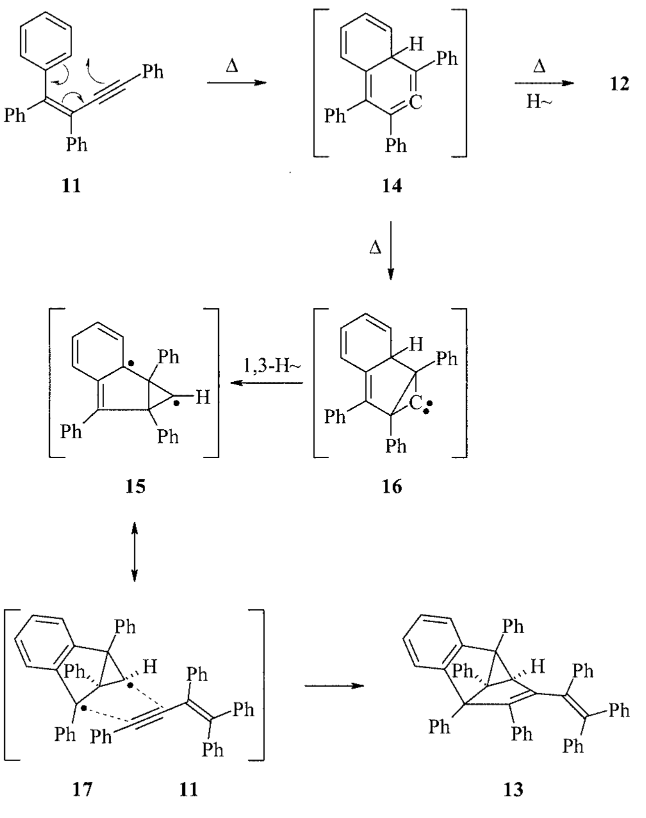


Figure 1. The molecule of compound **13** in the crystal; thermal ellipsoids are drawn at the 30% probability level

In the three-membered ring of the dimer **13**, the bond lengths are C4−C5 1.533(2), C4−C6 1.571(2), C5−C6 1.503(2) Å; the bond C1−C5 [1.586(2) Å] is somewhat longer than a standard single bond. A search of the Cambridge Database[12] revealed 22 ordered structures including a carbon skeleton as defined by C1−C8; the bond corresponding to C4−C6 was the longest, but showed a large scatter of 1.51−1.85 Å (mean 1.62 Å). This should be compared with the "standard" bond length of 1.509 Å, which was suggested by Allen[13] based on X-ray studies of small cyclopropane derivatives. Substituents about the double bond C7−C8 are coplanar [cf. torsion angle C6−C7−C8−C1 −1.2(2)°], but there is slight rotation about C13−C14 [C39−C13−C14−C45 9.4(3)°]. The molecular packing involves one short C−H···π contact from H47 to the centroid (Cg) of C21−26, with H···Cg 2.79, C−H···Cg 158°, operator 1 − *x*, 1 − *y*, 1 − *z*.

Mechanism of Formation of Semibullvalene 13

A mechanism to rationalize the formation of **13** is presented in Scheme 3. The isomerization/dimerization begins with the electrocyclic ring closure of **11** to generate the isobenzene **14**. This can either undergo the usual hydrogen shift to form the naphthalene **12**,[14] or collapse to the carbene **16**, formally a reverse of the classical Doering−Moore−Skattebøl allene synthesis. To generate a precursor suitable



Scheme 3. Mechanism of semibullvalene formation from a hexadienyne

for the formation of the ultimately isolated product **13**, a hydrogen shift is required (**16** → **15**), which can lead to the resonance-stabilized diradical **15** ↔ **17**. With this, the aromaticity of the benzene ring is restored, thus providing the driving force for this bond reorganization. In a final trapping step with the triple bond of the starting material **11**, the semibullvalene **13** is then produced.

In summary, depending on the type and degree of substitution, a remarkable molecular complexity can be generated under simple laboratory conditions from easily available precursors that contain a 1,3-hexadien-5-yne subsystem.

Experimental Section

General Remarks: 1,1,2,4-Tetraphenyl-1-buten-3-yne (**11**) was prepared as described in the literature[9] and characterized by the usual spectroscopic data. Pyrolyses were carried out in anhydrous toluene in heavy-walled glass ampoules that were sealed after several freeze-pump-thaw cycles and placed in a steel bomb tube for protection.

Pyrolysis of 11 at 360 °C: The starting hydrocarbon **11** (360 mg, 1.01 mmol) was dissolved in toluene (4 mL), and the solution was heated for 6 h. After cooling and opening of the ampoule, the solvent was removed in vacuo, and the residue was purified by chromatography (silica gel, pentane) and recrystallization (ethanol). Yield: 115 mg (32%) of 1,2,4-triphenylnaphthalene (**12**). M.p. 159 °C, ref.[10] m.p. 159−161 °C. The spectroscopic data are identical with those reported in ref.[10]

Pyrolysis of 11 at 290 °C: As described above, **11** (384 mg, 1.08 mmol) was pyrolyzed for 4 h. After workup (see above), 120 mg (31%) of the semibullvalene dimer **13** were obtained; recrystallization from pentane provided crystals suitable for X-ray structure determination (see below). M.p. 289 °C. ^{1}H NMR ($CDCl_3$, 400.1 MHz, int. TMS): δ = 7.24−7.28 (m, 1 H), 7.02−7.16 (m, 10 H), 6.93−7.01 (m, 12 H), 6.80−6.87 (m, 10 H), 6.60−6.65 (m, 4 H), 6.31−6.33 (d, J = 7.4 Hz, 2 H), 3.67 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz, int. TMS): δ = 142.79, 138.40, 137.96, 135.73, 130.92, 130.64, 130.51, 129.72, 127.44, 127.32, 127.22, 127.17, 126.77, 126.73, 126.53, 126.32, 126.04, 125.96, 125.92, 125.78, 125.14, 77.29 ppm. IR (diamond ATR): $\tilde{\nu}$ = 3082 (w), 3054 (w), 3021 (w), 2951 (w), 2926 (w), 2855 (w), 1573 (w), 1490 (m), 1467 (w), 1441 (m), 1155 (w), 1074 (m), 1027 (m), 913 (w), 841 (w), 785 (w), 756 (m), 696 (s) cm^{-1}. UV ($CDCl_3$): λ_{max} (log ε) = 329 nm (4.01), 240 (4.53). MS (EI, 70 eV): m/z (%) = 712 (100) [M$^+$], 621 (9), 545 (10), 467 (9), 367 (25), 356 (88), 339 (10), 279 (51), 265 (12), 239 (16), 178 (16), 167 (11), 138 (8). $C_{56}H_{40}$ (712.88): calcd. C 94.34, H 5.66; found C 93.71, H 5.72.

X-ray Structure Determination of 13: Crystal data: $C_{56}H_{40}$, triclinic, space group $P\bar{1}$, a = 9.712(3), b = 12.520(2), c = 17.608(2) Å, α = 75.852(8), β = 74.494(12), γ = 73.336(14)°, V = 1943.5 Å^3, Z = 2, μ(Mo-K_α) = 0.07 mm^{-1}, T = −100 °C. Data collection: A colorless prism ca. 0.65 × 0.4 × 0.25 mm was used to record 7259 intensities with a Siemens P4 diffractometer (Mo-K_α radiation, $2\theta_{max.}$ = 50°). Structure refinement: The structure was refined anisotropically on F^2 (program SHELXL-97),[15] to $wR2$ = 0.096, $R1$ = 0.041 for 505 parameters and all 6818 unique reflections; S = 0.90, max. $\Delta\rho$ = 0.18 e·Å^{-3}. Hydrogen atoms were included using a riding model. CCDC-236684 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] I. Dix, C. Doll, H. Hopf, P. G. Jones, *Eur. J. Org. Chem.* **2002**, 2547−2556.

[2] H. Hopf, H. Musso, *Angew. Chem.* **1969**, *81*, 704; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 680; and H. Hopf, unpublished results.

[3] U. Nüchter, H. Hopf, G. Zimmermann, V. Francke, *Liebigs Ann./Recueil* **1997**, 1505−1515. For a summary on the scope and mechanism of this cycloaromatization process, see: G. Zimmermann, *Eur. J. Org. Chem.* **2001**, 457−471.

[4] M. Christl, M. Braun, G. Müller, *Angew. Chem.* **1992**, *104*, 471−473; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 473−475.

[5] H. Hopf, H. Berger, G. Zimmermann, U. Nüchter, P. G. Jones, I. Dix, *Angew. Chem.* **1997**, *109*, 1236−1238; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1187−1190.

[6] W. J. Bailey, R. A. Baylouney, *J. Org. Chem.* **1962**, *27*, 3476−3478.

[7] R. R. Jones, R. G. Bergman, *J. Am. Chem. Soc.* **1972**, *94*, 660−661; cf.: R. G. Bergman, *Acc. Chem. Res.* **1973**, *6*, 25−31.

[8] For a recent review on the Bergman cyclization and related processes (Myers−Saito and Schmittel rearrangements, respectively) see: M. Winkler, H. H. Wenk, W. Sander in *Reactive Intermediate Chemistry* (Eds.: R. A. Moss, M. S. Platz, M. Jones, Jr.), John Wiley & Sons, New York, **2004**, chapter 16, pp. 741−794.

[9] F. Marcuzzi, U. Azzena, G. Melloni, *J. Chem. Soc., Perkin Trans. 1* **1993**, 2957−2960.

[10] R. Larock, Q. Tian, *J. Org. Chem.* **1998**, *63*, 2002−2009.

[11] For other benzannelated semibullvalenes see: E. Ciganek, *J. Am. Chem. Soc.* **1966**, *88*, 2882−2883 and refs. cited therein.

[12] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380−388.

[13] F. H. Allen, *Acta Crystallogr., Sect. B* **1980**, *36*, 81−96.

[14] M. Prall, A. Krüger, P. R. Schreiner, H. Hopf, *Chem. Eur. J.* **2001**, *7*, 4386−4394.

[15] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1997**.

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