Thermal cyclotrimerization of tetraphenyl[5]cumulene (tetraphenylhexapentaene) to a tricyclodecadiene derivative†

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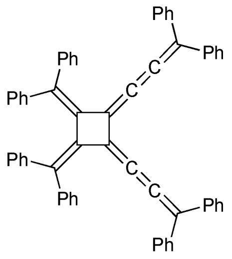
Tetraphenyl[5]cumulene (tetraphenylhexapentaene) underwent cyclotrimerization in refluxing toluene for 10–15 min to give a tricyclodecadiene derivative in 68% yield.

Cumulenic double bonds[1] have a wide variety of potentially reactive sites, which may lead to cyclic dimers, trimers and higher oligomers. A variety of carbocyclic systems possessing double bonds[2] exocyclic to the ring have been synthesized by thermal, photochemical and catalytic dimerization of allenes and higher cumulenes.[3] Although the cyclooligomerizations of ethylenes, acetylenes, allenes and butatrienes have been widely investigated,[4] only few examples are known of cyclotrimerization of cumulenes. Early studies showed that allenes trimerize at 130–200 °C in benzene to give isomeric cyclic trimers,[5] and butatrienes afford [6]radialenes upon transition metal catalyzed cyclotrimerization.[6] However, no reports are known for the trimerization of hexapentaenes, except for the oxidative cyclotrimerization of hexapentaene-extended quinocumulene.[7] In a broader sense, thermal reactions of higher cumulenes have been studied only in limited cases, presumably due to instability of these highly unsaturated compounds in atmospheric oxygen. On the other hand, although the reactions of aryl-substituted allenes[8] and butatrienes[9] have been investigated extensively, only few reports were found on the reactions of aryl-substituted higher cumulenes.[10] We report here the thermal cyclotrimerization of tetraphenylhexapentaene to a tricyclodecadiene derivative.[11]

It has been reported earlier that nickel-catalyzed reaction of tetraphenylhexapentaene proceeded smoothly at room temperature to afford the head-to-head (C_2–C_3) dimer[12] **3** as the main product with no formation of a trimer and that of hexapentaenes bearing bulky alkyl-substituents produces either the head-to-tail dimers or the dimers at the central C=C double bonds (C_3–C_4).[13] In contrast, thermal dimerization of tetra-*tert*-butyl[5]cumulene at 200 °C produces a C_3–C_4 dimer,[13,14] whereas tetramethyl[5]cumulene dimerizes at a lower temperature to give a C_1–C_6 dimer.[15] Thus, the known thermal and catalytic dimerizations of [5]cumulenes occur regioselectively.



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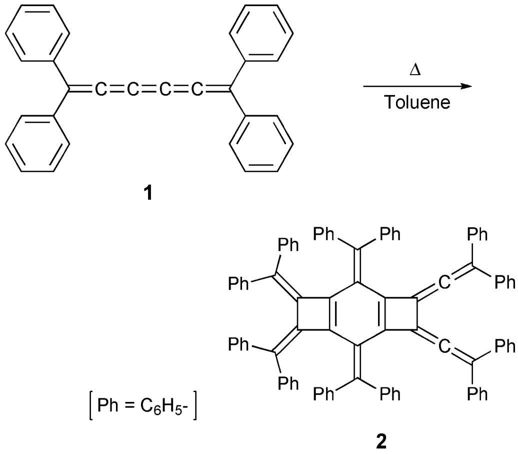
As the cyclooligomerization of [5]cumulenes has importance in organic synthesis because this reaction provides access to novel compounds of potential theoretical and synthetic interests, therefore, we have studied the thermal reaction of tetraphenylhexapentaene. When a solution of hexapentaene **1**[13] in toluene was heated at 110 °C for 10–15 min, the color of the solution changed from deep red to reddish purple due to the formation of the novel tricyclodecadiene derivative, **2** (Scheme 1).‡ As shown in Table 1 a minimum of 13.1 mmol L^{-1} of hexapentaene **1** in solution is needed to afford the trimer **2**. The reaction with a concentration lower than this does not occur even on refluxing for a longer period of time (entry 4), which leads to uncharacterized gummy materials. Experiments with higher than 30.8 mmol L^{-1} of hexapentaene show almost the same results (entry 1).

The thermal trimer **2** reported here is very stable towards light and air. However, when a CH_2Cl_2 solution of trimer



Scheme 1

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Table 1 Reaction of hexapentaene in refluxing toluene at different concentrations

Entry	**1**/mmol L^{-1}	Time	Yield of **2** (%)
1	43.6	10–15 min	68
2	30.8	10–15 min	67
3	13.1	3.0–3.5 h	25
4	6.5	Overnight	—

2 was subjected to prolonged irradiation of UV-Vis light, it resulted in slow decomposition of the compound. The electronic spectrum of the trimer shows a broad, strong absorption (λ_{max} = 555 nm, log ε = 4.64) tailing up to 700 nm, corresponding to the deep purple color in dichloromethane solution, indicating elongation of π-conjugation. The ^{1}H-NMR spectrum[12] of the trimer **2** shows an upper-field shift of the aryl protons (δ_H 6.5–7.6 ppm) due to the shielding effect of the closely situated neighbouring benzene ring. The ^{13}C-NMR spectrum also supports this phenomenon, as well as indicating the presence of allenic carbon in the molecule. The IR spectrum[16] confirms the presence of a C=C=C group, and contains a characteristic band at 1922 cm^{-1}. In order to determine the unique molecular structure of the trimer, its crystal structure was determined by X-ray diffraction analysis. Fig. 1 shows the molecular structure of **2** in the crystal; particularly noteworthy is the near-coplanarity of the central three fused rings (tricyclodecadiene). Molecular models of the trimer also demonstrate the planarity of the central three fused rings. It also shows that the compound has a C_{2v} symmetry and that each of the benzene rings is located at a very short distance, which is in turn in agreement with ^{1}H-NMR and ^{13}C-NMR spectra.

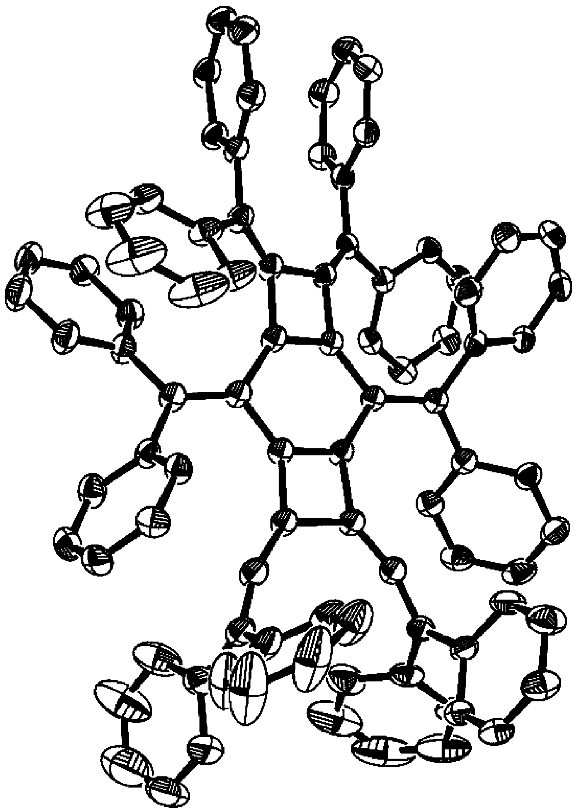
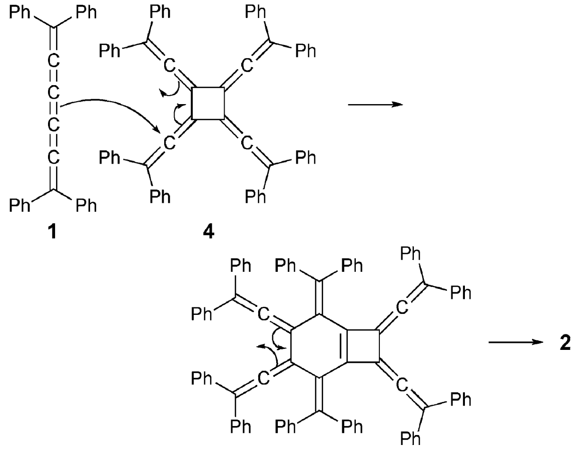


Fig. 1 ORTEP representation of the trimer **2**. Hydrogen atoms and one hexane molecule contained as a pair with **2** are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.



Scheme 2

From the X-ray crystal structure analysis, the allene residues are not linear (C=C=C angle is 163.67°) with C=C bond lengths of 1.29 and 1.32 Å, and a dihedral angle of 177.15° between the planes of its terminal C=C< groups. The two phenyl rings substituted at the different vinyl carbons are at a 114–116° angle to each other.

The formation of trimer can possibly be explained as due to a tandem process, *i.e.*, dimerization of hexapentaene **1** at the central C=C bond to afford an extended [4]radialene **4**, a subsequent [4 + 2] cycloaddition reaction, and electrocyclization (Scheme 2). Molecular orbital calculations[17] with optimized structures (B3LYP/6-31G*) suggest that the HOMO (−0.199 eV) of the radialene **4** and the LUMO (−0.091 eV) of **1** are very close to each other, so **4** may react with another molecule of **1** in a [4 + 2] manner[18] to give an intermediate which rearranges to trimer **2**.

These results suggest that thermal dimerization of tetra-arylhexapentaenes, as the trimer can form only through dimerization, follows the same regioselectivity of bulky alkyl-substituted [5]cumulenes[13,14] and may differ from transition metal catalyzed cyclodimerization of tetraphenylhexapentaene which takes place *via* a lateral cumulenic C=C bond to form unsymmetrical radialenes.[12]

The study of the chemical properties of the trimer **2** is currently underway and will be reported in due course.

Notes and references

‡ Experimental: 1,1,6,6-tetraphenyl-1,2,3,4,5-hexapentaene **1** (0.586 g, 1.54 mmol) was refluxed in toluene (50 ml) for 10–15 min. Evaporation of the solvent, separation by column chromatography and recrystallization from EtOAc–hexane afforded nice purple crystals of **2**, 0.392 g (0.343 mmol, 67% yield), mp 168–170 °C (decomp.).

Crystal data for trimer **2**: empirical formula, $C_{90}H_{60}{\cdot}C_6H_{14}$: M = 1227.64, crystal dimensions 0.60 × 0.50 × 0.40 mm, monoclinic, space group $P2_1/n$, a = 13.1788(5), b = 15.5047(5), c = 33.564(1) Å, α = 90, β = 93.516(1), γ = 90°, V = 6845.3(4) Å^3, Z = 4, T = 123.1 K, D_c = 1.191 g cm^{-3}, μ(Mo-Kα) = 0.067 mm^{-1}, F(000) = 2600, $2\theta_{max}$ = 55.00°, λ = 0.7107 Å, 67 937 reflections collected, 15 612 unique (R_{int} = 0.029), 10 774 observed (I > 2.0σ(I)) reflections, 925 refined parameters, R = 0.0690, wR = 0.1990, S = 1.348. The structure was solved by direct methods and expanded using Fourier techniques.[19]

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