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Review Commentary

Strained hydrocarbons from cyclic diynes—preparation and reactivity[†]

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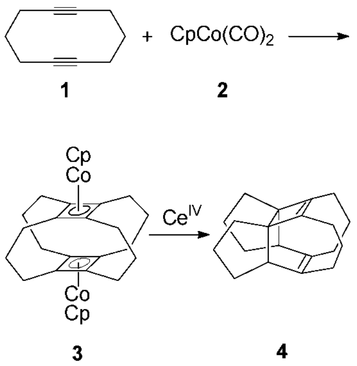
ABSTRACT: The reaction of cyclic diynes with either $CpCo(CO)_2$ or $AlCl_3$ yielded strained hydrocarbons in which a Dewar benzene or a tricyclo[4.2.0.0^{2,5}]octa-3,7-diene frame is bridged by hydrocarbon chains. The photochemistry and thermochemistry of these species are discussed. Results of quantum chemical calculations (DFT, CASPT2) are used to discuss the thermochemistry of four different fourfold bridged tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes. Depending on the bridging mode, either a Cope-type rearrangement or a ring opening reaction is preferred. Copyright © 2002 John Wiley & Sons, Ltd.

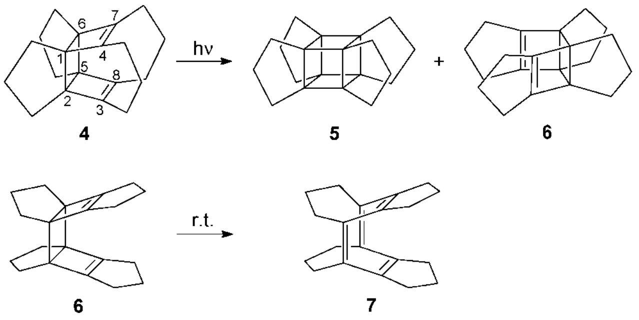
KEYWORDS: strained hydrocarbons; cage compounds; alkynes; photochemistry; thermal rearrangements; DFT calculations

INTRODUCTION

More than 50 years ago, Reppe *et al.*[1] discovered the metal-supported oligomerization of acetylene. This finding marked an important point in catalysis. Reppe *et al.*'s studies have been extended by others to substituted alkynes and to nitriles by using various metal templates.[2] The most important syntheses were trimerizations of alkynes to benzene[3] and pyridine derivatives.[4]



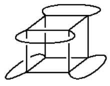
Scheme 1



Scheme 2

We became interested in this field by the serendipitous finding that cyclic diynes of medium ring size yield superphanes with metal-stabilized cyclobutadiene rings as building blocks (Scheme 1),[5] when treated with $CpCo(CO)_2$ or related reagents.

The resulting superphane **3** afforded in good yields the cage hydrocarbon **4**. The latter species are reacted with various electrophiles. By irradiation of **4** the propellacubane **5** was isolated in 10% yield in addition to the isomer **6**.[6] The latter species rearranged slowly at room temperature to the fourfold bridged cyclooctatetraene **7** (Scheme 2).



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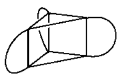

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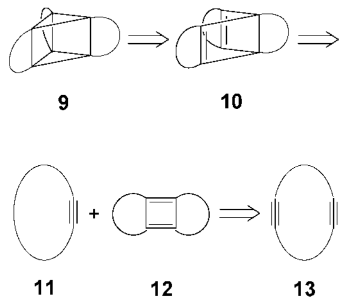
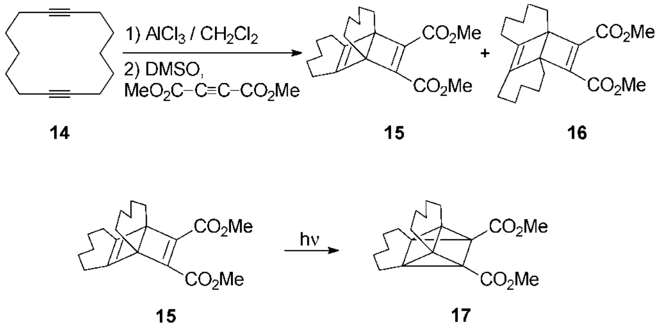


Scheme 3

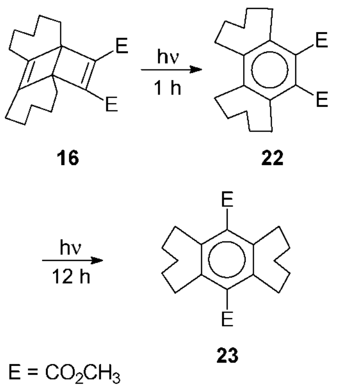


Scheme 4

The reactions shown in Scheme 2 initiated several investigations in our group: (i) we tried to synthesize other propellaprismanes such as **8** and **9**[7] and (ii) we investigated various bridged tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes with respect to their thermochemistry and photochemistry.

ON THE WAY TO PROPELLA[3$_n$]PRISMANES

One possible pathway to synthesize a propella[3$_n$]prismane is shown in Scheme 3 in a retrosynthetic approach starting from a cyclic acetylene **11** or **13** via a threefold bridged Dewar benzene **10**. To synthesize the desired threefold bridged Dewar benzenes from alkynes as suggested in Scheme 3, we made use of a procedure first reported by Schaefer and co-workers[8] and later modified by Hogeveen *et al.*[9]

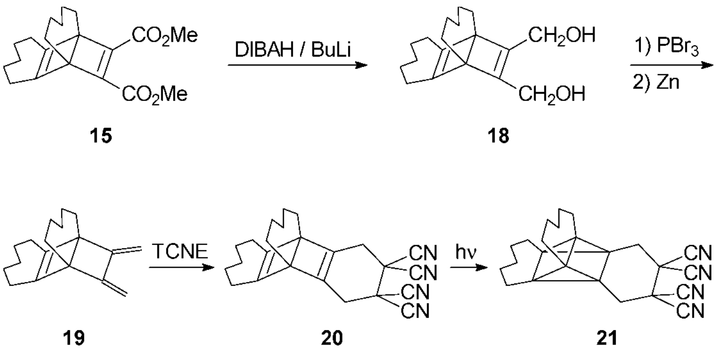


Scheme 6

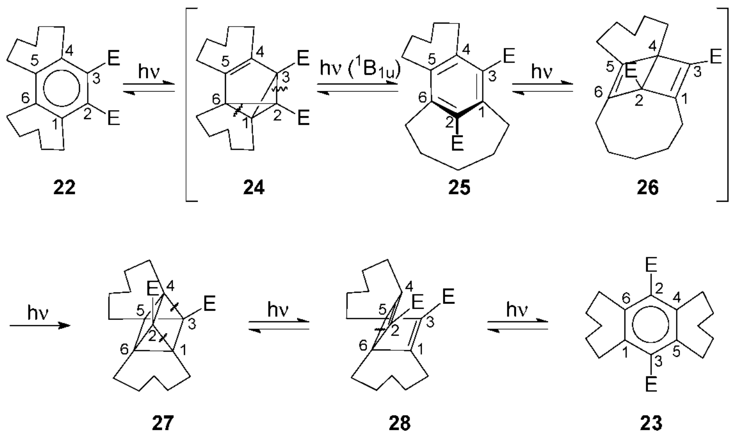
The reaction of 1,8-cyclotetradecadiyne (**14**) with $AlCl_3$ in methylene chloride and subsequently with dimethyl acetylenedicarboxylate (DMAD) yielded a mixture of the bridged Dewar benzenes **15** and **16** in a ratio of 1:1 (Scheme 4).[10] The irradiation of **15** produced the expected prismane **17**.[10] Its structure was investigated in more detail[11] by means of X-ray studies on single crystals.

To introduce the third bridge as shown in **9** we prepared in a classical way the bis(exomethylene) derivative **19** by reducing **15** to the diol **18** (Scheme 5). This was followed by the bromination to the dibromide and subsequent elimination.[12] The reaction of the triene **19** with tetracyanoethylene (TCNE) yielded the threefold bridged Dewar benzene **20**, which was converted to the threefold bridged prismane **21**[12] in a photochemical step.

The irradiation of **16** brought some surprises.[11–13] The central bond was cleaved to the corresponding twofold bridged phthalic ester **22** by irradiation for 1 h. A prismane derivative was not detected. When we continued the irradiation for a longer period (12 h) we were able to isolate the twofold bridged terephthalic ester **23** in 50% yield (Scheme 6).



Scheme 5

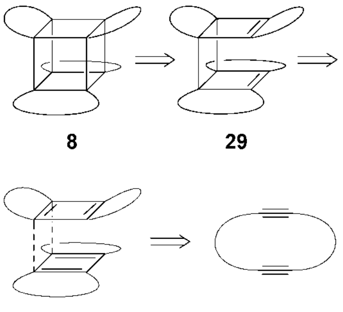


E = CO_2CH_3

Scheme 7

This reaction also took place in the case of phthalate esters with two hexamethylene bridges and one tetramethylene and one pentamethylene bridge. To rationalize the light-induced rearrangement we inferred the mechanism presented in Scheme 7. For the first step we assume an excitation of **22** to the $^1B_{2u}$ state[14] to yield the highly strained benzvalene derivative **24**.

Ring opening of **24** as shown in Scheme 7 yielded the *meta*-cyclophane **25**. Owing to the pentamethylene chain between C-1 and C-6 the carbon atom at position 2 is bent out of the plane towards position 4.[15] Excitation of **25** into the $^1B_{1u}$ state[14] is expected to result in the Dewar benzene derivative **26**. This latter species is estimated to be less strained than the former. Further irradiation of **26** yielded **27**. This step ought to be favored owing to a reduction of strain. The structure of **27** was verified by spectroscopic means and by X-ray investigations on single crystals.[11] Further irradiation of **27** yielded **28** by opening bonds C-1—C-2 and C-3—C-4, the only opposite bonds which are not stabilized by electronic effects or by bridges. The resulting Dewar benzene derivative **28** reverted to the most stable isomer, the terephthalate ester derivative **23**.[11–13]

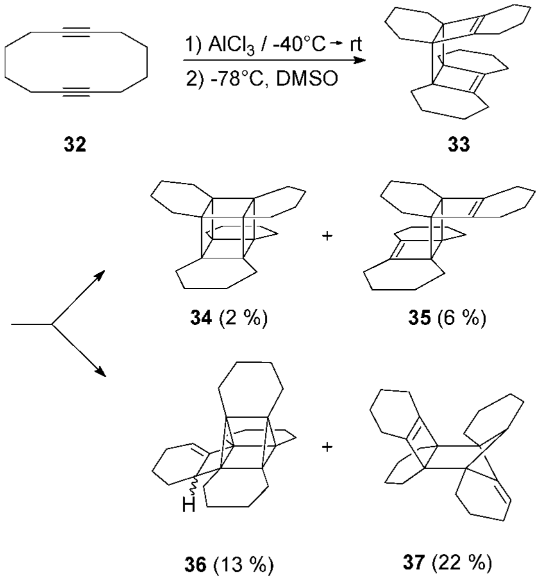


Scheme 8

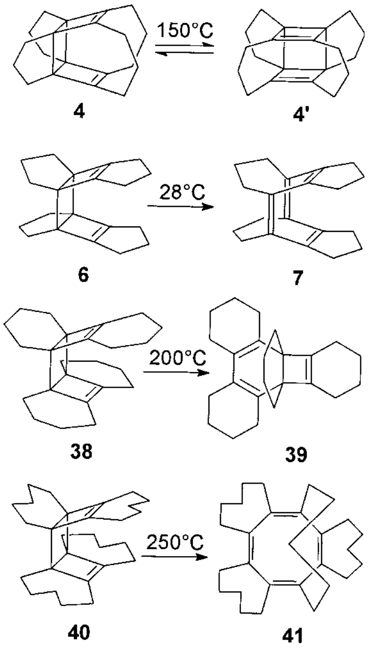
THE SYNTHESIS OF PROPELLA[4_4]PRISMANE

Our investigations were also aimed at the synthesis of **8**, an isomer of **5** with (averaged) D_{2d} symmetry. Scheme 8 illustrates a retrosynthetic route using the disconnection approach by starting with a cyclic diyne **31**.

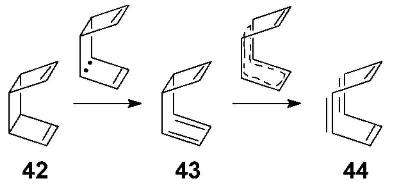
The key reaction of this approach is the cubane formation from **29** to **8**. According to literature reports,[16] however, this step seems unlikely to occur.[17] To investigate this matter in more detail we explored the photochemistry of octamethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene and found a rich photochemistry.[18] Among other products we detected octamethylcubane.[19] The yield of this product was, however, very low (1%). Nevertheless, we prepared the fourfold bridged tricyclo[4.2.0.0^{2,5}]octa-3,7-diene derivative **33** by dimeriza-



Scheme 9



Scheme 10



Scheme 11

tion of 1,7-cyclododecadiyne (**32**) in the presence of $AlCl_3$/DMSO (Scheme 9).[20] The minor product of the irradiation process was the fourfold bridged cubane derivative **34** among other highly strained hydrocarbons **35–37** (Scheme 9).[18]

ON THE THERMAL REARRANGEMENTS OF FOURFOLD BRIDGED TRICYCLO[4.2.0.$0^{2,5}$]-OCTA-3,7-DIENES

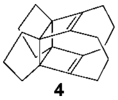
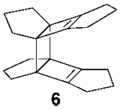
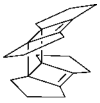
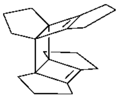
While studying the thermolysis of multiple bridged tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene derivatives such as **4** and **6**,[6] we investigated the thermal behavior of **38** and **40** (Scheme 10).[20] Whereas **4** preferred a Cope rearrangement,[6] the isomer **6** rearranged slowly at room temperature by cleaving two bonds to yield the fourfold bridged cyclooctatetraene **7**.[8] The congeners **38** and **40** had to be heated to 200–260 °C in order to rearrange to **39** and **41**, respectively.[20] To understand the difference in thermal behavior of these hydrocarbons, we explored the various possible mechanisms of thermolysis by means of quantum chemistry. All calculations were carried out with the Gaussian 98 package of programs.[21] We used the hybrid Hartree–Fock/density functional theory (DFT) method:[22] UB3LYP/6–31G*//UB3LYP/6–31G*. The geometric parameters were optimized using analytical gradient procedures. All stationary points of the potential surface were characterized by their second derivatives. In addition, we performed a multiconfigurational approach. We chose complete active space self-consistent field (CASSCF)[23] calculations. To include the effect of dynamic electron correlation[24] we used a multireference second-order perturbation treatment (CASPT2)[25,26] based on CASSCF wavefunctions. For these latter calculations we used the geometric parameters of the tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene (C8) core derived by the DFT procedure. The following model was used: CASPT2N(8,8)/6–31G*//U3LYP/6–31G*. To check the accuracy of both procedures we explored the stationary points for the thermal rearrangement of tricyclo-[4.2.0.$0^{2,5}$]octa-3,7-diene (**42**) to cyclooctatetraene (**44**) via bicyclo[4.2.0]octa-2,4,7-triene (**43**) (Scheme 11). The results obtained by the two procedures are compared with the experimental results in Table 1. The agreement between theory and experiment is excellent.

For **4** we considered a Cope rearrangement to **4′** (Scheme 10) and a ring opening reaction via a diradical intermediate. The DFT results revealed for the Cope reaction an activation energy $E_a = 19.6\,\text{kcal mol}^{-1}$ (1 kcal = 4.184 kJ), whereas the activation energy was $68.9\,\text{kcal mol}^{-1}$ for the bond breaking reaction. For the structural isomer of **4**, **6**, the activation energy for the Cope rearrangement was calculated to be $36.4\,\text{kcal mol}^{-1}$. For the biradical ring opening reaction an activation energy of only $27.2\,\text{kcal mol}^{-1}$ was found. The results of the DFT calculations for possible Cope rearrangements or ring opening reactions of **4, 6, 45** and **46** are compiled in Table 2. It is seen that the Cope rearrangement is only favored for **4**, whereas all the other

Table 1. Comparison between the experimental results ($H_{\text{rel}}^{\text{exp}}$) and the results of calculations (DFT, CASPT2N) for the rearrangement of **42** to **44** (the relative energies are given in kcal mol^{-1})

Species	$H_{\text{rel}}^{\text{exp}}$	$H_{\text{RT}}^{\text{DFT}}$	E^{CASPT2}
42	0	0.0	0.0
TS (**42** → **43**)	31	33.4	33.2
43	−41	−42.5	−40.9
TS (**43** → **44**)	20	18.0	21.2
44	−47	−51.9	−46.8

Table 2. Calculated (DFT) activation energies (kcal mol^{-1}) for the Cope rearrangement and ring opening reaction of **4, 6, 45** and **46**

Compound	Cope	Ring opening
 **4**	19.6	68.9
 **6**	36.4	27.2
 **45**	26.4	24.6
 **46**	31.4	22.3

isomers prefer a ring opening process via a biradical transition state. We ascribe this preference for the Cope rearrangement in the case of **4** to the close proximity of both double bonds. The distance between the center of the double bonds is predicted to be 2.72 Å for **4**. For **6, 45** and **46** those values are 2.99, 3.13 and 3.06 Å, respectively.

The relative low activation energies for the ring opening reaction (22–27 kcal mol^{-1}) are traced back to the relative high strain energy (DFT, isodesmic reactions) of **6, 45** and **46**. Owing to angle strain the difference in strain energy between **4** on one side and **6, 45, 46** on the other side is between 39 and 49 kcal mol^{-1}.

For **6** the calculation predicts a one-step mechanism, whereas for **45** and **46** the bicyclo[4.2.0] system is predicted to be the final product (**46**) or the intermediate (**45**) on the way to the fourfold bridged cyclooctatetraene.[5] These results are in line with the experimental findings summarized in Scheme 10.

CONCLUSION

The reaction of cyclic diynes in presence of $AlCl_3$ with dimethyl acetylenedicarboxylate (DMAD) produced new twofold bridged Dewar benzenes. They allowed us not only to isolate a threefold bridged [3]prismane derivatives but also to unravel a sequence of photochemical steps which led from a twofold bridged *o*-phthalate ester to a twofold bridged terephthalic ester.

By studying possibilities of how to prepare a fourfold bridged [4]prismane with (averaged) D_{2d} symmetry, we found a new access to fourfold bridged tricyclo[4.2.0.0^{2,5}]octa-3,7-dienes. The photochemistry of these species revealed a new entrance into cage hydrocarbons. We found two different pathways for the thermochemistry by means of quantum chemical calculations: a degenerate Cope rearrangement or a bond breaking reaction to a bicyclo[4.2.0]octadienyl diradical which finally produces a fourfold bridged cyclooctatetraene.

Acknowledgements

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