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Generation and Transformation of the [3.3.1]Propellane Skeleton by Thermal Rearrangements

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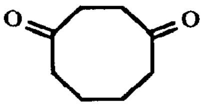
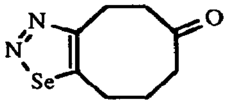
Abstract: In a sequence of unexpected thermal rearrangements the strained monocyclic alkyne **4** is transformed into the tricyclic system **5** which yields in a flash vacuum pyrolysis again a monocyclic compound **10**.

In the course of our investigations on transannular bond formations in strained ring systems[1] we found an unespected thermal isomerization of 5-methylenecyclooctyne (**4**) to tricyclo $[3.3.1.0^{1,5}]$non-2-ene (**5**). The cycloalkyne **4** was easily accessible from 1,4-cyclooctanedione (**1**) by applying the "selenadiazole method".[2] The reaction of the disemicarbazone of **1** with selenium dioxide led to the 1,2,3-selenadiazole **2**; simultaneously, the second semicarbazono group was split off by hydrolysis.[3] A Wittig reaction with methyltriphenylphosphonium bromide converted **2** into **3**.[4] Alkyne **4**[5] was generated by pyrolysis of **3** on copper powder at 175 °C and 0.5 Torr. The raw product **4** contained already small amounts of the propellane **5**. A carefully directed transformation **4** → **5** could be obtained at 210 °C or in a flash vacuum pyrolysis.



1



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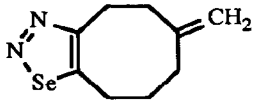

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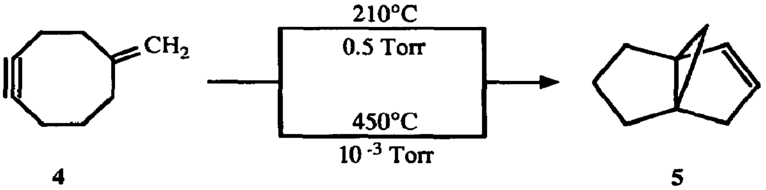
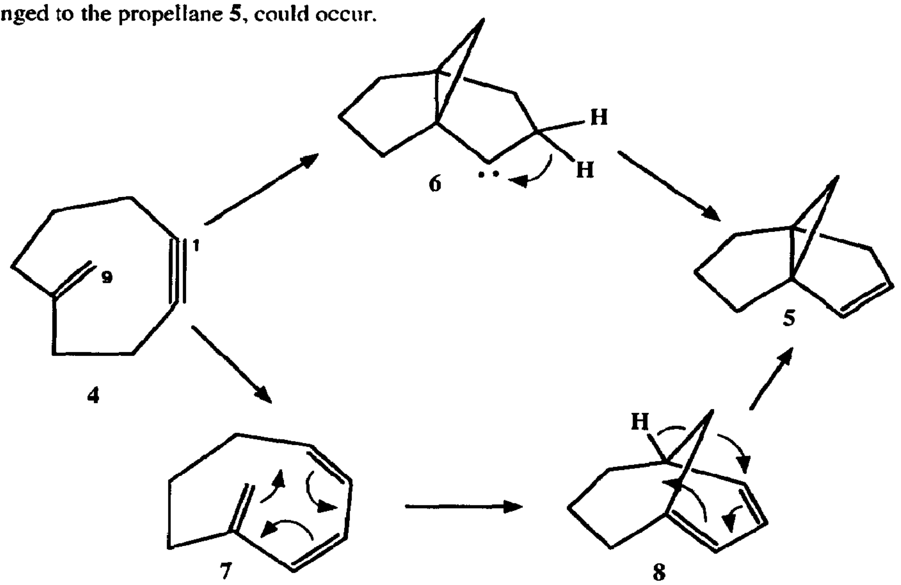


4 **5**

Principally two pathways can be conceived for a mechanistic rationalization. An initial bond formation between C-1 and C-9[6] in **4** would lead to the generation of the 3-membered ring in the intermediate carbene **6**.; the final product **5** can then be formed by a 1,2-H shift. The AM1 calculation[7] predicted for this route an activation barrier $\Delta H^{\neq} \geq 44$ kcal·mol^{-1}. The short half-life of **4** at 200 °C rules that mechanism out, even though the entropy term $T\Delta S^{\neq}$ is not known.[8] An alternative route involves the isomerization of **4** to the triene **7**, a well-known process in the thermal chemistry of strained cyloalkynes.[2] Subsequently an electrocyclic ring closure [π^6s] **7** → **8** and a hydrogen shift, in which the anti-Bredt olefin **8** is rearranged to the propellane **5**, could occur.



The AM1 calculation as well as a force field calculation (MMX)[9] are consistent with this reaction sequence. The enthalpies of formation ΔH_f calculated by the latter method are shown in Figure 1. (The ΔH_f values obtained in the AM1 calculation were very similar; a difference of more than 10 % was only obtained for the propellane **5**).

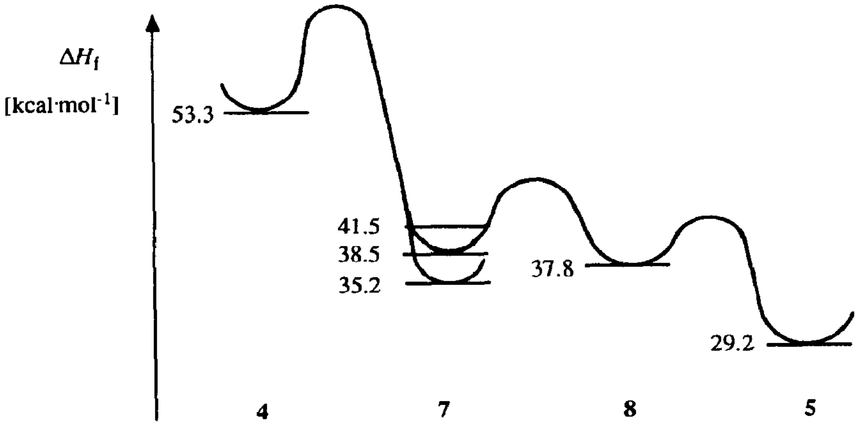
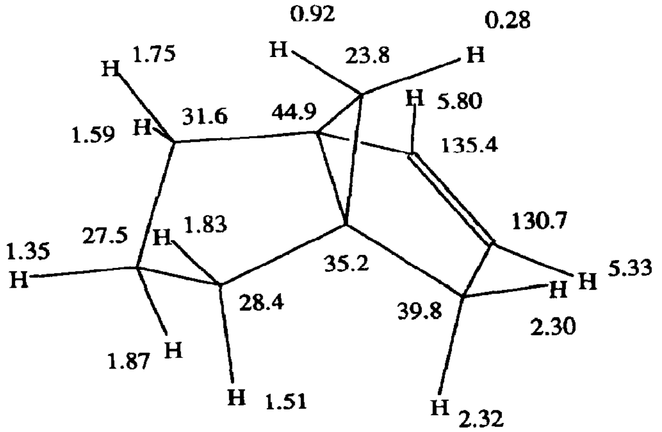


Figure 1. Calculated[9] enthalpies of formation ΔH_f for the reaction sequence **4** → **7** → **8** → **5**

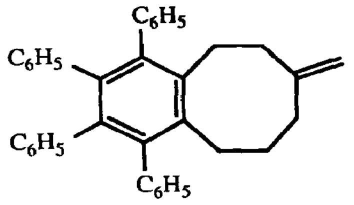
According to the calculations the triene **7** can exist in three conformers. The energy-lowest conformer **7a** has a geometry that is appropriate to a [π^2a + π^4a] reaction leading to a tricyclic system of the type [4.3.0.0^{1,3}]; however such a process could be detected by no means. The conformer **7b** with ΔH_f = 38.5

kcal·mol^{-1} on the other hand has a much shorter distance between C-1 and C-9, namely 362 pm versus 467 pm for **7a**. Thus, we assume a reaction of **7b** → **8** irrespective of the lower population of **7b** in comparison to **7a**.[10] An experimental proof for the proposed intermediates **7** and **8** was not possible, but this is not very surprising since the first step **4** → **7** should be the slowest one.

Applying ^{1}H,^{1}H-COSY and ^{1}H,^{13}C-shift correlated NMR spectra and NOE measurements we were able to perform a complete assignment of the ^{1}H and ^{13}C chemical shift values of **5**.



Propellane **5** is - as well as the parent compound tricyclo[3.3.1.0^{1,5}]nonane[11] - stable at the air; contrary to the precursor **4** it does not react with tetraphenylcyclopentadienone. Therefore small portions of **4**, eventually present in the trap of the pyrolysis apparatus, can be easily removed; the cycloadduct **9**[12] forms in toluene a quantitative precipitate whereas **5** remains in solution.



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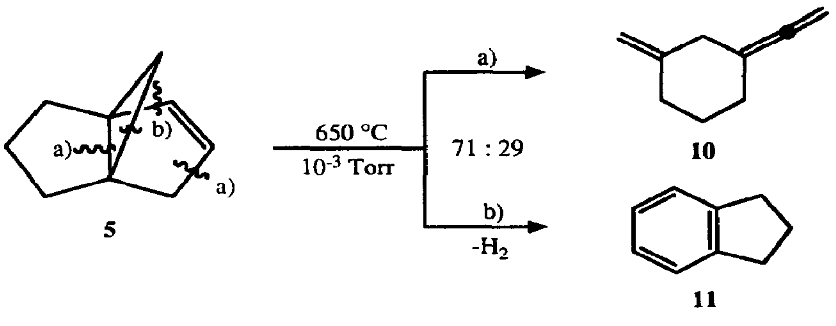
Flash vacuum pyrolysis of **5** yielded 1-ethenylidene-3-methylene cyclohexane (**10**);[13] indane was



5

10

11

observed as a by-product. Route a) reminds of the rearrangement of cycloalkynes to vinylidenecycloalkanes;[14] route b) refers to the reaction sequence bicyclo[3.1.0]hex-2-ene → 1,4-cyclohexadiene → benzene[15]. However, due to the ties bound by the trimethylene chain a different mechanism has to be valid.

Acknowledgments
We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie for the financial support.

References and Notes

1. Detert, H.; Antony-Mayer, C.; Meier, H. *Angew. Chem.* **1992**, *104*, 755-757; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 791-792.
2. Meier, H. *Adv. Strain Org. Chem.* **1991**, *1*, 215-272 and references therein.
3. **2**: Yield 48 %, mp 54 °C; ^1H NMR ($CDCl_3$): δ = 3.45 (m, 2 H, 4-H), 3.20 (m, 2 H, 9-H), 2.75 (m, 2 H, 5-H), 2.35 (m, 2 H, 7-H), 1.85 (m, 2 H, 8-H); ^{13}C NMR ($CDCl_3$): δ = 212.6 (C-6), 159.4 / 158.9 (C-3a, 9a), 47.7 / 39.1 (C-5,7), 25.7 / 25.7 / 23.1 (C-4,8,9).
4. **3**: Yield 63 %, oil; ^1H NMR ($CDCl_3$): δ = 4.76 / 4.71 (AB, 2 H, exo-CH_2), 3.25 (m, 2 H, 4-H), 3.06 (m, 2 H, 9-H), 2.44 (m, 2 H, 5-H), 1.90 (m, 2 H, 7-H), 1.79 (m, 2 H, 8-H); ^{13}C NMR ($CDCl_3$): δ = 160.8 / 159.3 (C-3a, 9a), 148.4 (C-6), 114.3 (exo-CH_2), 40.3 / 31.6 / 31.6 / 26.7 / 25.1 (C-4,5,7,8,9).
5. **4**: Yield 45 %, oil; ^1H NMR ($CDCl_3$): δ = 4.93 (s, 2 H, exo-CH_2), 2.48 (m, 2 H, 4-H), 2.27 (m, 2 H, 3-H), 2.18 (m, 4 H, 6,8-H), 2.03 (m, 2 H, 7-H); ^{13}C NMR ($CDCl_3$): δ = 153.0 (C-5), 113.5 (exo-CH_2), 94.3 / 93.9 (C-1,2), 41.8 (C-4), 35.9 (C-6), 34.7 (C-7), 22.6 (C-3), 20.5 (C-8).
6. Compare the formation of the anti-Bredt enol ethers in lit.[1]
7. Version MOPAC V 6.0.
8. For $\Delta G^{\neq}$ = 44 kcal·mol^{-1} and T = 200 °C the half-life of **4** would amount to 171 d.
9. Version PCMODEL V 4.0, (Serena).
10. Due to energetic as well as steric reasons the energy-highest conformer **7c** (ΔH_f = 41.5 kcal·mol^{-1}) is again less suitable for the generation of a transannular bridge.
11. Warner, P.; LaRose, R.; Schleis, T. *Tetrahedron Lett.* **1974**, *15*, 1409-1412.
12. **9**: Yield 191 °C; ^1H NMR ($CDCl_3$): δ = 7.10 (m, 10 H, Phenyl-H), 6.74 (m, 10 H, Phenyl-H), 4.73 / 4.72 (AB, 2 H, exo-CH_2), 2.78 (m, 2 H, 1-H), 2.69 (m, 2 H, 6-H), 2.19 (m, 2 H, 2-H), 2.03 (m, 2 H, 4-H), 1.49 (m, 2 H, 5-H).
13. Oil; ^1H NMR ($CDCl_3$): δ = 4.66 / 4.65 (AB, 2 H, exo-Methylene), 4.58 (m, 2 H, Ethenylidene), 2.81 (m, 2 H, 2-H), 2.18 (m, 4 H, 4-H, 6-H), 1.64 (m, 2 H, 5-H); ^{13}C NMR ($CDCl_3$): δ = 203.5 (sp-C), 147.0 (C-3), 107.9 (exo-Methylene), 104.4 (C-1), 73.4 (CH_2, Ethenylidene), 39.4 (C-2), 34.5 (C-4), 30.5 (C-6), 27.6 (C-5).
14. Meier, H.; Schmitt, M. *Tetrahedron Lett.* **1989**, *30*, 5873-5876.
15. Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*, Academic Press **1981**, p. 130.

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