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Generation of Octamethylcuneane and Octamethylcubane from *syn*-Octamethyltricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene.

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Irradiation of *syn*-octamethyltricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene (**4**) at temperatures between 20°C and 30°C with high pressure mercury lamp (125 W) in n-pentane yields as main product octamethylcuneane (**6**) and in traces octamethylcubane (**5**).

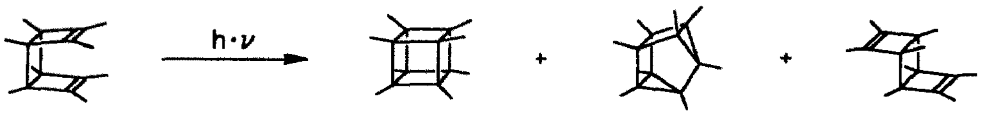
Recently we found that the irradiation of the fourfold bridged tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene **1** yields the propellacubane **2** and its valence isomer **3**[1].

1 **2** **3**

These results differ from those reported for unbridged species such as octamethyltricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene (**4**)[2,3]. In this case it was reported that the irradiation of **4** under various conditions does not yield octamethylcubane (**5**)[2,3].

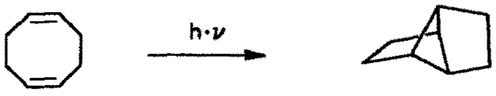
The difference between the photochemistry of **1** and **4** we have ascribed to two effects: the closer proximity of the double bonds in **1** (2.65 Å) as compared to **4** (3.0 Å) and a different sequence of the π-MOs for **1** as compared to **4**[4]. The latter was based on MO calculations and PE studies on model substances where we could compare the through bond effect of an ethano and propano group[5].

Since we were not quite satisfied with the results of the photochemistry on **4** we repeated the experiment. Irradiation of **4** in degassed n-pentane at 20°C to 30°C, with a high pressure mercury lamp (125 W) yields a mixture of at least three products. Column chromatography on silicagel with n-hexane afforded octamethylcuneane (**6**)[6,7] (10% yield), traces of **5**[8] and *anti*-trimethyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene (**7**).

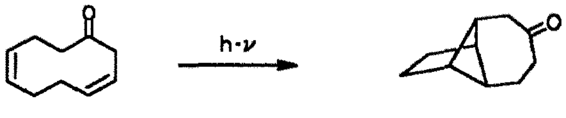


4 5 6 7

The formation of **6** is anticipated if one takes into account that the irradiation of 1,5-hexadiene-derivatives such as 1,5-cyclooctadiene (**8**)[9] or 3,7-cyclodecadiene-1-one (**9**)[10] yields mainly the "head to tail" products **10** and **11**, respectively.



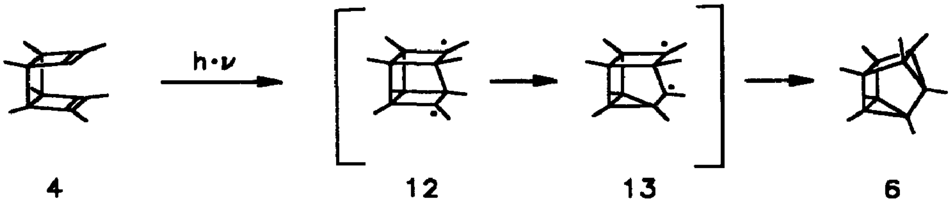
8 10



9 11

These findings have been rationalized empirically by assuming that in the ring closing process a biradical with a five-membered ring is formed (rule of five)[11]. Taking into account electronic (through bond interactions via ethano fragment) and steric effects (conformations with a staggered arrangement of the ethano bridge(s)) it was concluded that in **8** and **9** the "head to tail" products **10** and **11**, respectively should be preferred[12].

Assuming for the excited **4** as a first step a "head to tail" bond closure to **12** as shown in below leads via **13** to **6**.



The appearance of **5** in the reaction mixture indicates that the difference in activation energy for the "head to head" and "head to tail" product must be small[4c].

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7 Compound **6**: ^1H NMR (300 MHz, $CDCl_3$): 0.83 (s), 0.86 (s), 1.05 (s); ^{13}C NMR (75.46 MHz, $CDCl_3$): 6.24, 7.86, 8.69, 43.09, 43.81, 50.26.

8 Compound **5**: ^1H NMR (200 MHz, $CDCl_3$): 1.56 (s); ^{13}C NMR (50.32 MHz, $CDCl_3$): 6.87, 51.20.

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