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THERMOLYSIS OF *syn*- AND *anti*-TRICYCLO[4 2 0 0^{2,5}]OCTANE 1)

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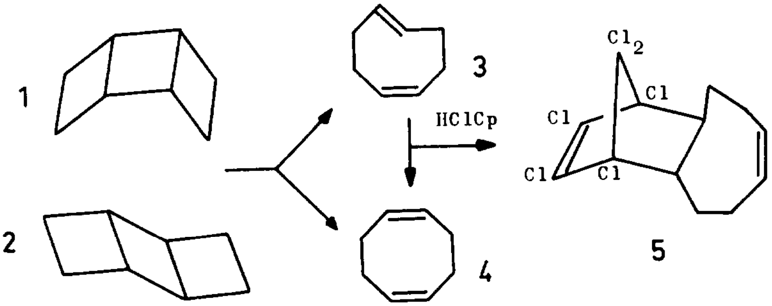
The thermolysis of **1** and **2** has been reported on by several groups 2) The only product isomeric with starting material was identified as *cis,cis*-cyclooctadiene **4** The fact that bicyclo[2 2.0]hexanes on heating mostly yield *cis,trans*-dienes 3) and that such a behaviour has actually been uncovered in case of a tetracyano-derivative of **2** 4) seemed enough justification to repeat these experiments more carefully

We have found that either **1** or **2** in the gas-phase as well as in solution leads thermally to both *cis,cis*- and *cis,trans*-cyclooctadiene Our results are explained by the following scheme which assumes a parallel formation of **3** and **4** both from **1** and **2** and a consecutive *trans*-*cis*-isomerization step **3** → **4** 5)



This scheme is supported by the following experimental facts.

a) Thermolysis of **1** or **2** in the gas-phase (195 °C and 220 °C, resp., about 170 torr, flow system) or in solution (C_4Cl_6, 150 °C, 5 min or 190 °C, 10 s) yields a mixture of **3** and **4** (about 3:5).

b) Thermolysis of **1** or **2** in hexachlorocyclopentadiene (HClCp) at 150 °C gives rise to the formation of **5** and **4** 6) (about 3:5). **3** can be trapped by HClCp in the gas - phase as well

c) Thermolysis of **3** in the gas-phase (195 °C, about 170 torr, flow system) yields a mixture of **3** and **4** (about 3 1).

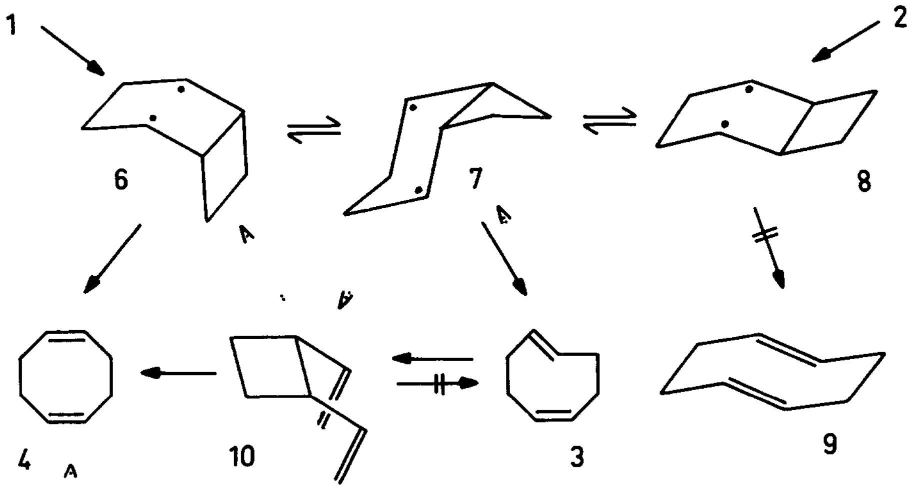
d) Heating of **3** in HClCp (150 °C) leads to **5**; no **4** can be observed (NMR-analysis, about 3% could have been detected).

3 has been characterized spectroscopically and by reaction with $AgNO_3$ (complex: mp 175 °C) 7), diphenyldiazomethane (formation of an adduct) 6), iodine (isomerization to **4**) 7) as well as by reaction with itself (dimer: mp. 120 °C) 6).

The single-inversion-pathway in the pyrolysis of bicyclo[2.2 0]hexanes is therefore, at least partially, obeyed by the tricyclooctanes, too. These stereochemical observations fit well into our present concept concerning thermal isomerization pathways in the bicyclo[2 2.0]hexane-, tricyclo[4 2.0.0^{2,5}]octane- and tetracyclo[4.4.0.0^{2,5} 0^{7,10}]decane-series 8). This concept demands a mechanism involving diradicals with lifetimes sufficient for allowing internal rotation. These diradicals are capable of undergoing rapid conformational changes which lead to a possibly established equilibrium between **6**, **7**, and **8**, the equilibrium concentrations being unknown. Stereoselective cleavage eventually yields **3** and **4**. We have been unable so far to detect **9** or polymers derived from it. 9)

A $(\sigma_2^s + \sigma_2^a)$-pathway does not find strong support, not only by the arguments given earlier 3) but also by the fact that thermolysis of a "pterodactylane" **A** 10) (in our opinion a crucial substrate for elucidating the mechanism of bicyclo[2.2.0]hexane-isomerization) does not give products which are in line with this concerted alternative. A "forbidden" $(\sigma_2^s + \sigma_2^s)$-fission is even more unlikely.

A pathway leading from **1** or **2** to *cis*-1,2-divinylcyclobutane **10** and subsequently by a quasi-chair-Cope process to **3** can be excluded 5,11). **10** is reported to rearrange thermally (100 °C) in low yield (3%) to a product which has not yet been ruled out to be *cis,trans*-cyclooctadiene **3** 11). We have thermolyzed **10** under the same conditions as in case of **1** (195 °C, flow system, about 170 torr). The only detectable product (> 95% by NMR-analysis) is **4**. The full arrows in the scheme represent processes which are sufficient to account for the observed products, the dotted arrows may be looked at as additional pathways.



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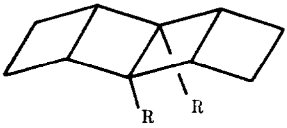

A R = $COOCH_3$

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