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COOPERATIVE [2+2+2] CYCLOADDITION REACTIONS IN POLYQUADRICYCLANYLIDENE [n]ROTANES - MODEL STUDIES IN TRIS-SPIRO(C_7H_6)SYSTEMS

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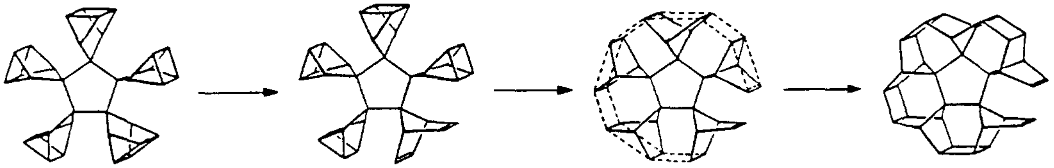
Summary: Starting from biquadricyclanylidene, two substrates with three closely placed quadricyclanylidene units have been synthesized. In thermolysis and DMAD cycloaddition reactions, multiple intercyclic and potentially cooperative bond formation ($[_\pi 2+(_\sigma 2+_\sigma 2)_2]$; $[_\pi 2+(_\sigma 2+_\sigma 2)_3]$) has been realized.

In the (C_7H_6) pentamer **2**, derived from the pentaquadricyclanylidene[5]rotane **1**, according to calculations and model studies1), the geometrical/stereoelectronic and energetic situation is rather favourable for an 18 electron2) cooperative, multiple domino type transformation (**3**) into the polycycle **4**. In the specifically prepared tris-spiro C_7H_6 systems **12b/14** this type of intercyclic, potentially cooperative bond formation has now been studied.

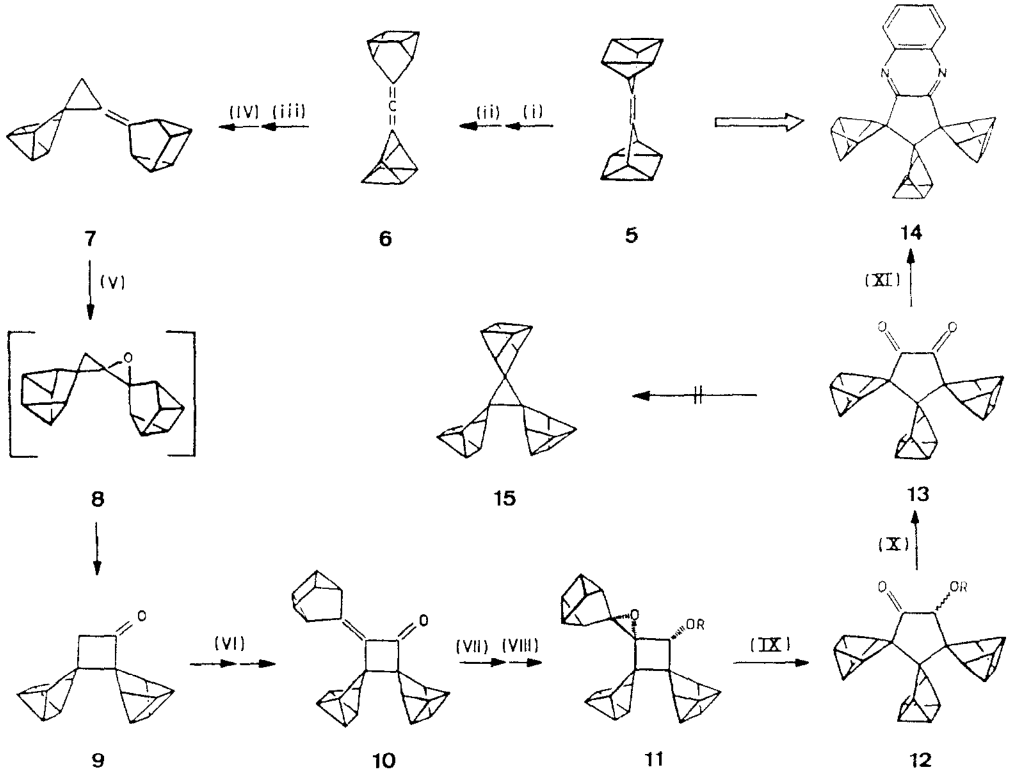


1 **2** **3** **4**

The synthesis of **12b/14**3), as outlined in Scheme 1, starts out from biquadricyclanylidene **5** and features oxaspiropentane → cyclobutanone4) and oxaspirohexane → cyclopentanone5) rearrangements as key steps. By conventional methodology, **5** was transformed into the allene **6** (m.p. 183°C (dec.), 69%)6) and the latter into **7** (m.p. 92-93°C, 71%). After epoxidation of **7**, only cyclobutanone **9**, arising from migration of the higher substituted cyclopropane C-C-bond in the transient **8**7), was detected and isolated by chromatography (m.p. 124°C, 60%)8). Condensation of **9** with quadricyclanone yielded ca. 65% of **10** (m.p. 177-178°C) which, however, could not be oxidized to the corresponding epoxyketone9), a potential precursor of diketone **13**. For that reason, the latter was approached via **11/12**. For the reduction of **10** to the allylic alcohol (m.p. 190°C (dec.), 80%) the system $NaBH_4/CeCl_3$10) proved to be advantageous. Epoxidation lead to a ca. 4:1 mixture of the syn/anti-epoxyalcohols, from which the syn-isomer **11a** (R=H) was separated by crystallization from diethylether (m.p. 156°C, 69%). While the rearrangement of **11a** to **12a** (R=H) at 60°C ($LiClO_4$, benzene) was accompanied by substantial decomposition, the methylether **11b** (R=CH_3)

rearranged almost quantitatively to **12b** (R=CH_3) (m.p. 102-103°C) at room temperature, effective chelation being obviously helpful[11]. Under the same conditions, the acetate **11c** (R=Ac) was stable up to 120°C. Swern oxidation of **12a** to the orange diketone **13** was straightforward (94%). Purification and handling of **13** were, however, complicated by its light-sensitivity[12]. Under the influence of daylight, a complex mixture of products arises with no trace of trisquadricyclanylidene[3]rotane **15**. Diketone **13** was therefore transformed into the stable quinoxaline **14** (m.p. 215°C, 62%).

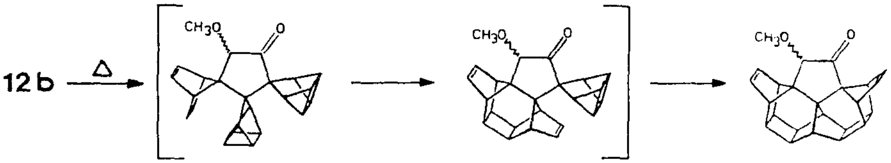
Scheme 1



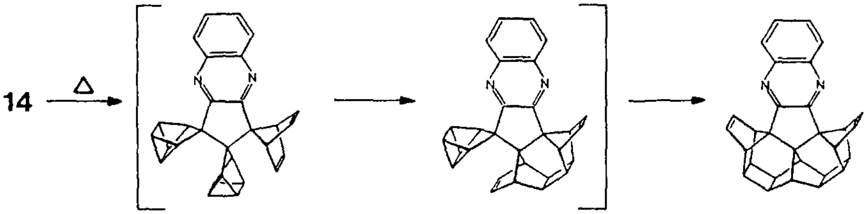
(i) $CHCl_3$/50% NaOH/TEBA-Cl, 4 h; (ii) n-BuLi/ether,-10°C, 1.5 h; (iii) 1 eq. $CHCl_3$/50% NaOH/TEBA-Cl/CH_2Cl_2, 4 h; (iv) Li/tBuOH/ether, refl., 6 h; (v) m-CPBA/0.5M aq. $NaHCO_3$/CH_2Cl_2, 0°C, 2 h; (vi) LDA/THF, 0°C, 40 min; quadricyclanone, 60°C, 3 h; (vii) $NaBH_4$/0.4M-$CeCl_3 \cdot 6\,H_2O$/CH_3OH, 20°C, 10 min; (viii) m-CPBA/0.5M aq. $NaHCO_3$/CH_2Cl_2, 0°C, 5 h; (ix) $LiClO_4$/benzene, 60°C (20°C), 30 min; (x) $(COCl)_2$/DMSO/CH_2Cl_2/Et_3N, -60°C; (xi)o-phenylenediamine/CH_3OH, refl., 4 h.

In contrast to the findings with earlier studied systems (e.g. **4**,**13** in [1]), selective opening of one of the quadricyclane units in **12b**/**14** to give e.g. **16**/**19** could not be achieved. Under proven conditions (i.a. $PdI_2[Sb(C_6H_5)_3]_2$, (p-$C_6H_4Br)_3NSbCl_6$[13])), rapid and complete polymerization occurred. Upon thermolysis of **12b**/**14** at 150°C (ca. 10^{-1}M degassed benzene solution, total conversion after 4-5 d), ca. 30% of the undecacyclic isomers **18** (m.p. 151°C) and **21** (m.p.

280°C (dec.)), resp., are formed besides polymers and no intermediate (**16**,**17**, **19**,**20**) was detectable (DC, ^{1}H-NMR). Rapid intercyclic interception of incipient diradicals could be responsible for the relatively high polymer content.

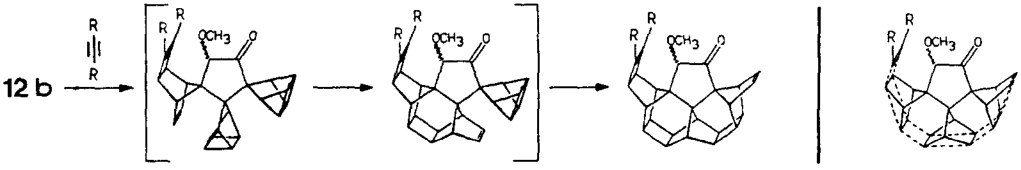


16 **17** **18**



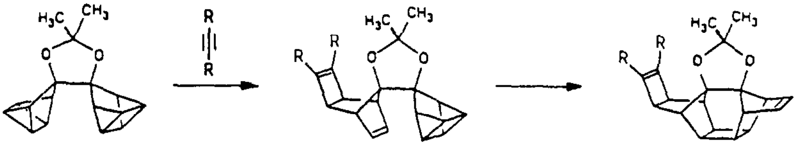
19 **20** **21**

In line with this explanation, product formation is clearly more selective in the reaction of **12b** with dimethyl acetylenedicarboxylate (DMAD) (5 equiv.) at 120°C or at 80°C (benzene). After total conversion (3 d at 120°C), ca. 70% of the dodecacyclic 1:1 adduct **24** (m.p. 248°C) were isolated (rest polymers). Also in the very slow reaction at 80°C, the intermediates **22**/**23** were not detected (DC, ^{1}H-NMR monitoring). Steric hindrance (as on the C=O side in **12b**) prohibits the addition of DMAD to **14** (up to 110°C, dec.).



$R=CO_2CH_3$ **22** **23** **24** **25**

With the formation of the three four-membered rings in **24**, a double domino-type $[_{\pi}2+_{\sigma}2+_{\sigma}2]$ cycloaddition has been realized. Its course in so far contrasts with the DMAD-addition to the ketal **26**, as in the latter case, at 60-65°C, the primary $[_{\pi}2+_{\sigma}2+_{\sigma}2]$ adduct **27** was kinetically stable and isomerized into **28** only at higher temperatures. Still, to view **24** as the result of a cooperative 14-



26 $R=CO_2CH_3$ **27** **28**

electron $[_{\pi}2+[_{\sigma}2+_{\sigma}2]_3]$ process (**25**)[14], attractive as it is in the context of multielectron pericyclic processes[15], remains speculative.

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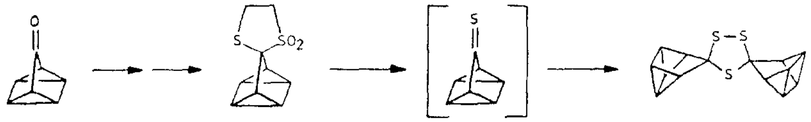
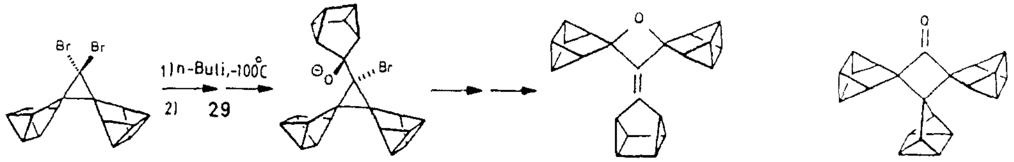


29 **30** **31** **32**

4) Attempts to prepare the cyclobutanone **36** from **33** via **34** resulted in the formation of the oxetane **35**.



33 **34** **35** **36**

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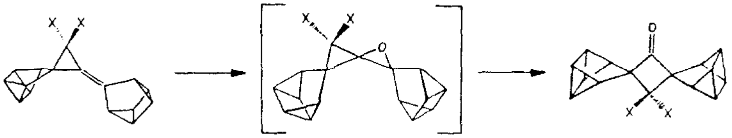
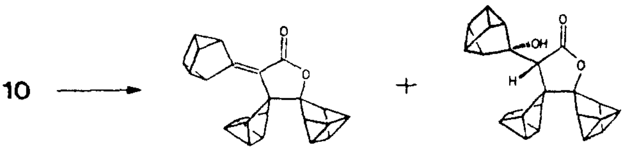


37 **38** **39**

9) Hydrogen peroxide in basic solution oxidizes **10** to a mixture of lactones **40** (60%) and **41** (25%); cf.7).



40 **41**

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