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CIS-TRIS-[2.2.2]-σ-HOMOBENZENE - SYNTHESIS AND THERMOLYSIS

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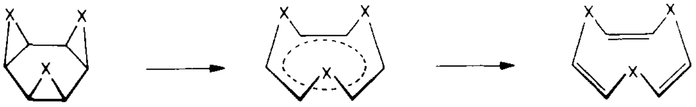
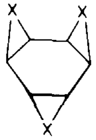
The cis-tris-[2.2.2]-σ-homobenzene 7 has been synthesised. From vapour phase thermolyses (400-500°C) it is concluded, that the $[_{\sigma}2_s+_{\sigma}2_s+_{\sigma}2_s]$-cycloreversion reaction is - at most - only a minor pathway in the thermal stabilisation of 7.

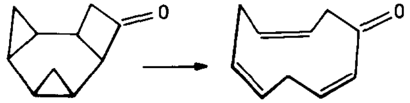
The cis-tris-[1.1.1]-σ-homobenzenes A (in contrast to the trans-isomers) have very favourable stereoelectronic prerequisites for thermal $[_{\sigma}2+_{\sigma}2+_{\sigma}2]$-cycloreversion (A→B→C)[1]. The resulting difference in kinetic stability between cis-/trans-pairs A/D is an important mechanistic criterium[2]. With

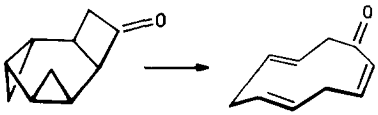




A B C D

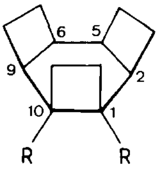
increasing size of the pericyclic transition states this kinetic differentiation should become less pronounced[3,4] - as indicated by the behaviour of the cis-/trans-ketones 1/3 (dis,dis,dis to Z,Z,Z-2 and dis,con,con to Z,E,E-4)[5]. For the experimental verification of the hypothesis, that for 12-mem-





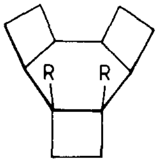
1 2 3 4

bered transition states the relative stability of cis-/trans-tris-[2.2.2]-σ-homobenzenes could even be reversed, problems were expected: With three four-membered rings participating early[6] trishomobenzenoid stabilisation (e.g. 19) is supposedly weak and hampered by steric compressions. With increasing



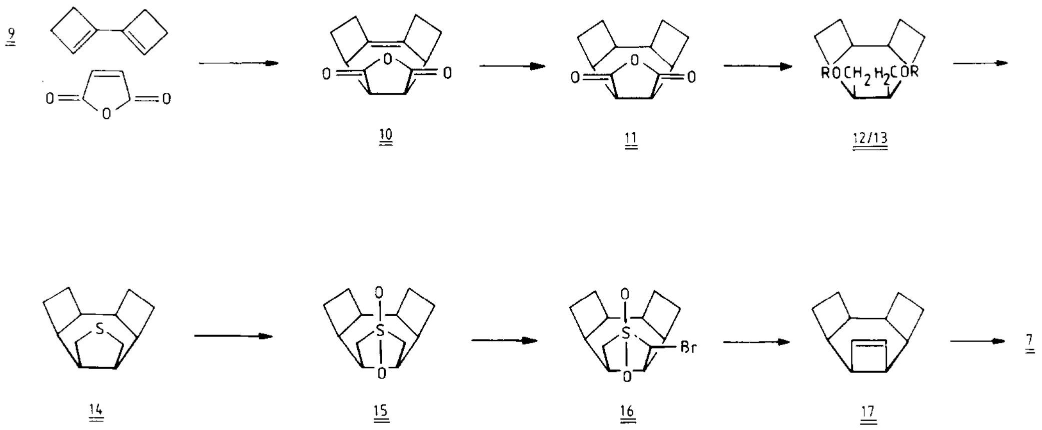
5 R = CN 6

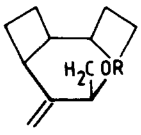
7 R = H 8



activation energies for the concerted cycloreversions homolytic processes will become competitive. In this regard the parent hydrocarbons 7/8 are better models than the dicyano-derivatives 5/6 [7].

The route devised for the synthesis of 7 (8) [8] was patterned on the published procedure for 5/6. The trans-compound, however, is not accessible by this route, since bicyclobutenyl 9 [9] adds maleic anhydride exclusively in the endo-fashion to afford the 1:1-adduct 10 [7] (with improved yield of 60%) as well as decomposition products of 9 . Reduction to give 11 (Pd/C (10%), diethyl ether, 20°C, 95%), to 12 (R=H, LAH/tetrahydrofuran, 75%, m.p. 59-60°C) and esterification (CH_2Cl_2/triethylamine/mesyl chloride) to the bismesylate 13 (80%, m.p. 60-61°C) are straightforward. In the reaction of 13 with Na_2S (boiling ethanol) besides 14 (57%, b.p. 60°C/10^{-2}Torr) minor side products are formed, one of which is 18 (5%). Bromination of the sulphone 15 (96%, m.p. 65-66°C) according to Corey-Block [10] (n-BuLi, -78°C, BrCN) gives the oily and highly unstable 16 (76%), which without detailed characterisation is transformed into 17 (potassium t-butylate, boiling THF, 29%, purified by chromatography). The low yield in the Ramberg-Bäcklund-step 16 → 17 probably reflects the steric compression in the product. After hydrogenation (Pd/C) the cis-tris-[2.2.2]-σ-homobenzene 7 ((1α,2α,5α,6α,9α,10α)-tetracyclo[$8.2.0.0^{2,5}.0^{6,9}$]dodecane) is isolated (v.p.c., Carbowax, 120°C, 100%) as a colourless oil The ^{13}C NMR spectrum (C_6D_6) consists of two signals (δ= 31.9, $J_{C,H}$= 136 Hz, tert.C, δ=24.4, $J_{C,H}$=133 Hz, sec.C). The ^1H NMR spectrum ($CDCl_3$) showing broad singlets (δ= 2.43) for the six cyclohexane protons and two multiplets for the methylene protons (δ= 2.04 (exo), 1.92 (endo)) is temperature invariant down to -70°C. Presumably the high torsional strain in 7 with all rings planar is minimised - as shown for 5/6 by X-ray analysis [7] - by chair-like distortion of the six-membered ring and by twisting the three four-membered rings - fast processes even at - 70°C (C_{3v}-symmetry).





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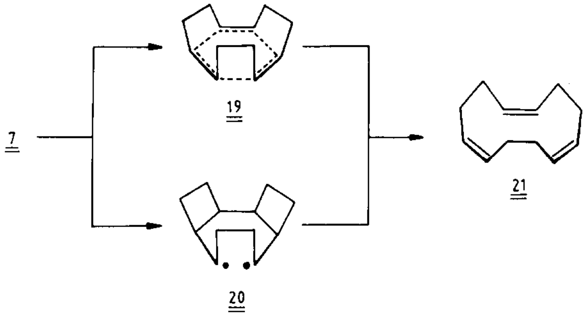
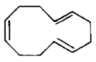
For the $[_{\sigma}2+_{\sigma}2+_{\sigma}2]$-cycloreversion 7 → 19 → 21 a ΔH‡-value of 50-52 kcal/mole, indicative of isomerisation temperatures between 450-500°C, was estimated based on additive increments and neglecting H/H-interactions. In view of the instability of the cyclododeca-1,5,9-triene 21 (and its isomers 22-24) in this temperature range as published by Rienäcker and Balcioglu[11], analytical complications had to be expected. Under the previously described vapour phase pyrolysis conditions 7 is transformed to a minor extent at 400°C, to 35% at 420°C, to 54% at 450°C and to 89% at 500°C. According to careful GC/MS-(10% CM 20) and ^{1}H-NMR-monitoring (250 MHz) the thermolysates (Tab.) are mainly composed of highly volatile, unidentified fragments. In addition the cyclododecatrienes 21 - 23, the trivinylcyclohexanes 27 - 30 and at high conversion the divinylcyclooctenes 25/26 have been identified.

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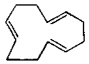
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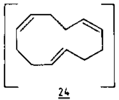
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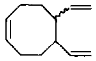
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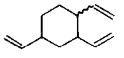
cis : 26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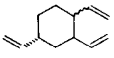
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Tab. Composition (%) of the Thermolysates of 7

	7	21	22	23	25	26	27-30	fragments
420°C	65	2	1	1	-	-	3	30
450°C	46	2	2	2	1	1	5	40
500°C	11	1	2	2	1	1	12	70

It was ascertained from the literature[11] and by control experiments with the trienes 21-24 that the $C_{12}H_{18}$ - products 22-30 (at least to a great extent) arise from the Z,Z,Z-triene 21. Since the fragments do not stem from

21 (or **22**-**24**), the percentage of Z,Z,Z-**21** is at best 15-20%. Obviously, for the *cis*-*tris*-[2.2.2]-σ-homobenzene **7** (as for **5**) the 3σ → 3π-isomerisation is no longer the favoured stabilisation pathway. For that reason, the question concerning the formation of **21** - concerted via the trishomobenzenoid transition state **19** with cooperative scission of the three cyclobutane C-C-bonds, stepwise via e.g. the diradical **20**, - looses much of its significance. It should be noted, that within the same temperature range the trioxide **A** undergoes the $[_{\sigma}2_{s}+_{\sigma}2_{s}+_{\sigma}2_{s}]$-cycloreversion quantitatively.

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