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STEREOELECTRONIC ASPECTS OF THE $[_\pi2+_\sigma2]$-PHOTOCYCLOADDITION REACTION** - $[_\pi2+_\sigma2]$-PHOTOCYCLOADDITIONS IN THE TETRACYCLO$[4.4.0.0^{2,10}.0^{3,7}]$DEC-4-ENE SYSTEM

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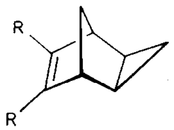
In agreement with expectations efficient ethylene/cyclopropane cycloadditions have been observed in derivatives of tetracyclo$[4.4.0.0^{2,10}.0^{3,7}]$dec-4-ene upon direct excitation.

In line with the intrinsic properties of the participating bonds the ethylene/cyclopropane (oxirane, aziridine) photocycloaddition ($[_\pi2+_\sigma2]$) is strongly geometry-dependant: It is efficient in the exo-tricyclooctene framework A, not however in the endo-isomer [1,2]; it has no chance against the $[_\pi2+_\pi2]$-reaction in the homobarrelene B [3], occurs uniformly with the exo-cyclopropane ring in the bishomobarrelene C [4] and it generally proceeds only intramolecularly [4,5]. A comparable ethylene/cyclobutane cycloaddition did not take place even under favourable conditions (D)[5]. For the series E [5], 3,8-bridged analogues of A, the expectations were such, that, independant of the mechanism, the increase in the interplanar angle ω from F to H and thereby in the transannular π/σ-interaction [6,7] would favour the transannular bond formations. And indeed, such transformations were realised in G [5] (not G',G'' [8]) but not in F [7].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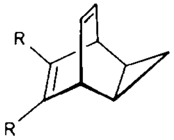
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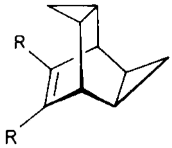
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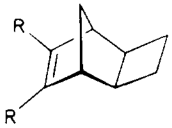
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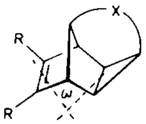
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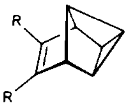
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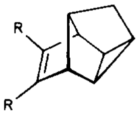
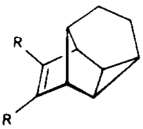

G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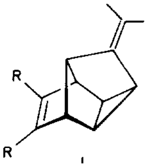
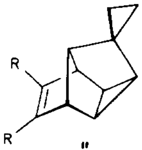
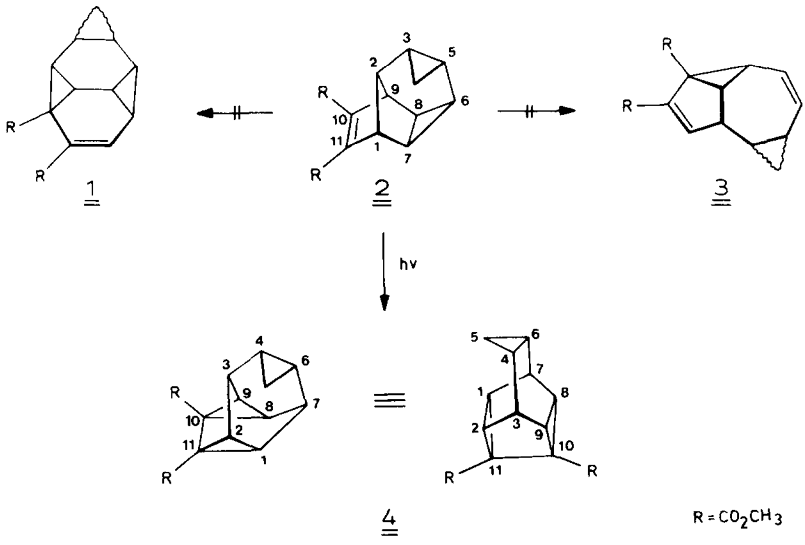
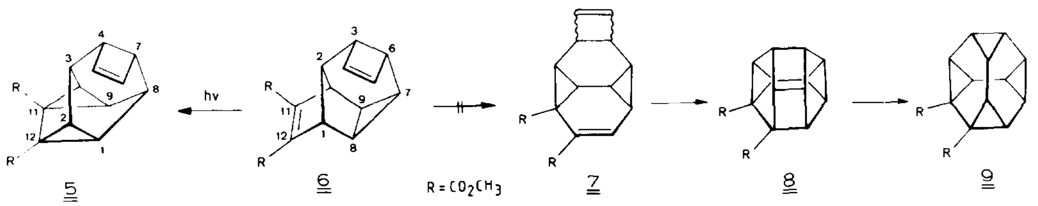

G'


G''

With the synthesis of the pentacyclic diesters 2/6 we now have models for the next higher homologue H (tetracyclo$[4.4.0.0^{2,10}.0^{3,7}]$dec-4-ene; the diester ($R=CO_2CH_3$) is not available from dihydrobarrelene and dimethyl acetylenedicarboxylate (ADM)[9]) whereby the ester groups guarantee favourable excitation [10]. 2 (dimethyl pentacyclo$[5.4.0.0^{2,9}.0^{3,5}.0^{6,8}]$undec-10-ene-10,11-dicarboxylate) was obtained in 80-85% yield by [2+2+2]-addition of ADM to homobarrelene (boiling xylene; colourless oil, m/e= 260 (M^+), $\lambda_{max}(CH_3CN)$= 235 nm (ε= 5050)).([2+2+2]-adducts were also obtained with dicyanoacetylene and with phenyltriazolinedione, not, however, with maleic anhydride or 1,2-bistolylsulphonylethylene [11]). Under the same and varied conditions the Nenitzescu hydrocarbon affords only a moderate yield (15%) of 6 (dimethyl pentacyclo$[6.4.0.0^{2,10}.0^{3,6}.0^{7,9}]$dodeca-4,11-diene-11,12-dicarboxylate), the cyclobutene unit probably causing side reactions [12]. 6 had to be separated from polymeric material by chromatography (colourless oil, m/e= 272 (M^+), λ_{max}(CH_3CN)= 235 nm (ε= 5040)). With regard to the scope of homo-Diels-Alder-additions [9] it is worthy of note that bicyclo[2.2.2]octa-5,7-diene 2-one [13] did not react with ADM, dicyanoacetylene or N-phenyltriazolinedione (up to 200°C).

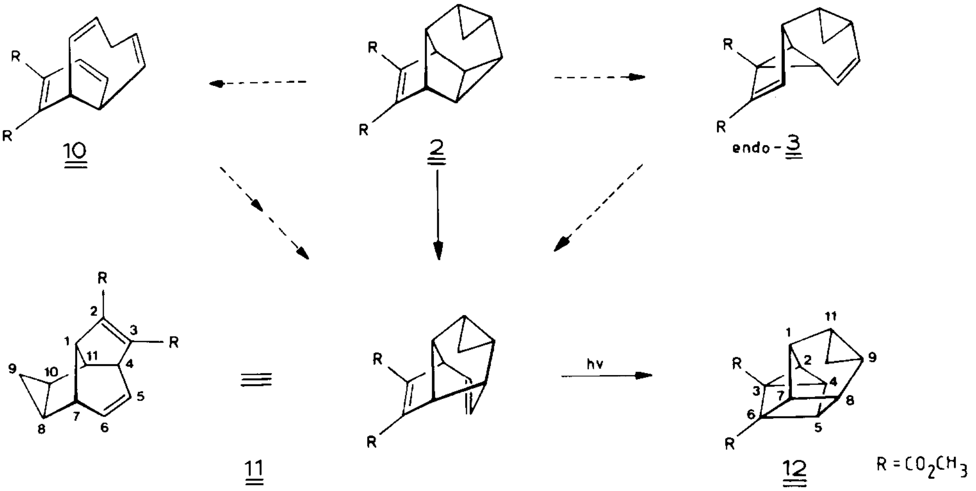
Upon direct excitation (10^{-3} to 10^{-4}M, N_2-sat. CH_3CN-solutions, 0°C, quartz-filter, high pressure Hg-lamp (150 W)) 2 is quickly and uniformly (TLC, ^{1}H-NMR) transformed into the crystalline, C_s-symmetrical [$_\pi2+_\sigma2$]-adduct 4 (dimethyl hexacyclo$[5.4.0.0^{2,11}.0^{3,9}.0^{4,6}.0^{8,10}]$undecane-10,11-dicarboxylate, m.p. 72°C, m/e= 260 (M^+)). Under these conditions 6 is isomerised with comparable selectivity (> 90% isolated) into crystalline 5 (dimethyl hexacyclo$[6.4.0.0^{2,12}.0^{3,10}.0^{4,7}.0^{9,11}]$dodec-5-ene-11,12-dicarboxylate, m.p. 81°C, m/e= 272 (M^+)). The hydrocarbons 4/5 (R=H) had been synthesised by other routes [14]. Qualitatively, the [$_\pi2+_\sigma2$]-additions in 2/6 are faster and more selective than in the lower homologues C. As in the latter sensitised excitation (acetone) affords only polymeric material. In view of the behaviour of





G,G'and G'' it is remarkable, that the cyclopropane ring in 2 does not induce concurrent formation of 1 and/or 3. endo-7, the (thermally certainly very labile) product of a 1,3-shift in 6, would be an attractive precursor of the bridged tris-σ-homobenzenes 8(9) 15).

Being interested in the scope of the [$_\sigma2+_\sigma2+_\sigma2$]-cycloreversion reaction 16) we also studied the thermal behaviour of 2, which has the structural elements of a cis-tris-[3.1.1]-σ-homobenzene (cf. the fast retro-Diels-Alder cleavage in lumibullvalene 17)). 2 is stable in solution up to at least 200^{o}C. Thermolysis in the vapour phase (450-500^{o}C) leads, however, to a selective transformation: The product, isolated in up to 90% yield (based on extent of conversion) is 11 (dimethyl tetracyclo[5.4.0.0^{4,11}.0^{8,10}]undeca-2,5-diene-2,3-dicarboxylate, oil, m/e= 260 (M $^+$), λ_{max}(CH_3CN) = 236 nm (ε= 4930)). The structure determined by NMR-analysis (^{1}H-, ^{13}C-) is supported by the photoisomerisation (direct excitation) to 12 (dimethyl hexacyclo[5.4.0.0^{2,4}.0^{3,6}.0^{5,8}.0^{9,11}]undecane-3,6-dicarboxylate, 80-88%, m/e= 260 (M $^+$)). endo-3



(followed by Cope Rearrangement) rather than 10 is considered to be an intermediate in the surprisingly selective isomerisation 2 → 11.

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