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TWO CONSECUTIVE CYCLOREVERSIONS OF *as*-HOMOBASKETENE
(PENTACYCLO[5.4.0.0^{2,5}.0^{3,9} 0^{4,8}]UNDECENE-10)

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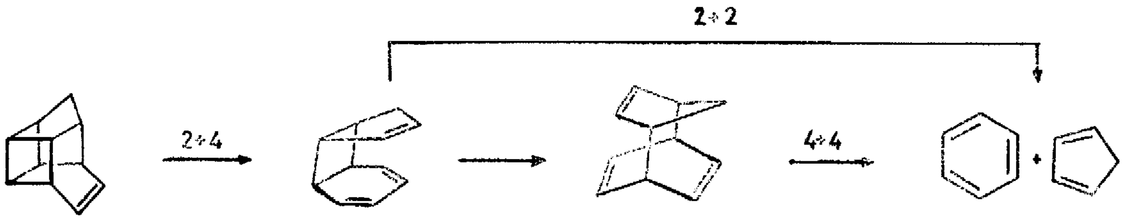
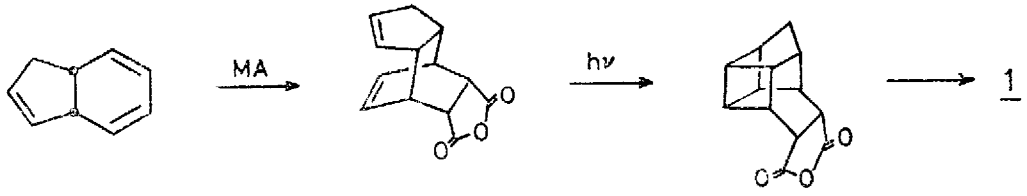
Our interest in cycloreversions yielding benzene and cyclopentadiene[1] led us to study the thermolysis of pentacyclo[5.4.0.0^{2,5}.0^{3,9} 0^{4,8}]undecene-10 (*as*-homobasketene) (1), a twofold cycloadduct of said components. In analogy to basketene[2] one would expect a primary (2+4)-cycloreversion to give *syn*-tricyclo[5.4.0.0^{2,6}]undeca-3,8,10-triene (2), which might either - as does its *anti*-isomer[3] - undergo a (2+2)-cycloreversion to benzene and cyclopentadiene or isomerize first via a Cope rearrangement to tricyclo[4.2.2.1^{2,5}]-undeca-3,7,9-triene (3)[4] and fragment further by a (4+4)-pathway. A one-step slicing of the molecule by concerted rupture of four bonds seems highly improbable as in terms of the frontier orbital approach[5] *both* fragments would need degenerate pairs of FOs.



1 2 3

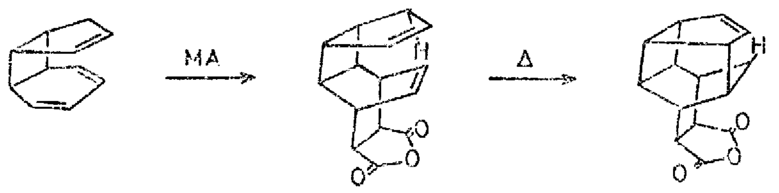
The synthesis of 1 was modelled after that of the parent compound[6], starting with the maleic anhydride adduct 4[7] of *cis*-8,9-dihydroindene. Photocyclisation in 10% acetone solution (Gräntzel 70 W low pressure mercury arc, vycor filter) produces the pentacyclic anhydride 5 [34%; mp 157°; pmr ($CDCl_3$), δ1.52 (2 methylene H, AB-system, J = 9.9 Hz, $\Delta\nu$ = 12.8 Hz), 2.0-3.1 (8 H, 3 m), 3.23 ppm (2 H, AB-system, J = 9 Hz, $\Delta\nu$ = 25 Hz, A-part split to d with J = 4.5 Hz, B-part split to d with J = 3 Hz); ν_{CO} (KBr), 1850, 1780 cm^{-1}; C 72.83, H 5.64], which after solvolysis in MeOH-HCl to the half ester was epimerized and saponified with aqueous NaOH. The resulting diacid on bis-decarboxylation with lead tetraacetate in pyridine-acetonitrile yielded *as*-homobasketene 1: 29%; mp 58-60°; pmr ($CDCl_3$), δ1.39 (2 methylene H, AB-system, J = 10.5 Hz, $\Delta\nu$ = 15.4 Hz, B-part split to t with J = 1.5 Hz), 2.0 (2 H, m), 2.4 (2 H, m), 2.7 (2 H, m), 3.1 (2 H, m), 6.20 ppm (2 olefinic H, AB-system, J = 8.3 Hz, $\Delta\nu$ = 24.1 Hz, A-part split to d with J = 6 Hz, B-part split to d with J = 4.5 Hz); C 91.83, H 8.24.



4 5

In perchlorobutadiene solution above 180° or on distillation in a stream of argon through a hot tube (>370°, ca. 18 sec residence time) homobasketene fragments cleanly to benzene and cyclopentadiene. In both cases the intermediancy of valence isomer 2 or 3 could not be detected. However, heating 1 with a 20 fold excess of maleic anhydride in *o*-dichlorobenzene at 180° for 30 hrs resulted in the formation of a 1:1 adduct to the $C_{11}H_{12}$ unit: 60%;

mp 201°; pmr ($CDCl_3$), δ1.05 (1 methylene H, B-part of AB-system, J = 15 Hz, split to d with J = 7 Hz), 2.1-2.9 (7 H, m), 3.0-3.6 (4 H, m), 5.99 ppm (2 olefinic H, narrow m); ν_{CO}(KBr), 1840, 1776 cm^{-1}; C 74.10, H 6.34. Surprisingly, the adduct displays only two olefinic protons in the pmr spectrum instead of the four in the expected trapping product 6. An inspection of a model reveals that the etheno- and the propeno-bridge in 6 are only 2.8 Å apart and ideally orientated for an intramolecular ene-reaction which, indeed, in a similar compound[8] occurs at 45°. On this basis we ascribe structure 7 to the trapping product, arising from an ene-reaction in the primary adduct 6. The proposed structure is supported by the strong shielding of one of the methylene protons (ca. 1.3 ppm relative to the other as calculated from the line intensities of the AB-half-spectrum) which is due to its contact with the π-cloud of the double bond and by the absence of prominent cycloreversion fragments $C_{11}H_{12}^+$, $C_6H_6^+$ and $C_5H_6^+$ in the mass spectrum. The fragmentation of *as*-homobasketene is thus shown to start with a (2+4)-cycloreversion to *syn*-tricyclo[$5.4.0.0^{2,6}$]undeca-3,8,10-triene (2), whereas the classification of the second step as a (2+2)- or (4+4)-process awaits further study.



2 6 7

The kinetics of the homobasketene fragmentation were followed by glpc in 0.4M dodecane solution versus tetralin as internal standard. The first order rate constants at 185.5, 187.4, 188.3 and 190.3° ($k_1 \cdot 10^5$ = 8.30± 0.07, 9.73 ±0.05, 10.8±0.1 and 12.5±0.1 sec^{-1}) fit the Arrhenius equation

$$\log k = (12.76 \pm 0.45) - (35300 \pm 1000)/2.303\cdot RT$$

from which the activation enthalpy $\Delta H^{\ddagger} = 34.4$ kcal/mol is obtained. This value exceeds the $\Delta H^{\ddagger}$ for the basketene opening[2] by only 5.4 kcal/mol, whereas both cycloreversions differ by ca. 16 kcal/mol in their calculated[9] heats of reaction. In fact, the (2+4)-cycloreversion of 1 turns out to be endothermic and the levelling of the activation enthalpies may be rationalized by the Hammond principle which calls for more strain release in the transition state for the opening of homobasketene as compared with the parent compound[10].

References and footnotes

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