The Thermolysis of Tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene, a New Entry into $(CH)_8$ Systems

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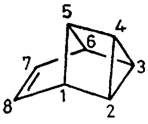
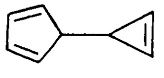
Summary At 270—500 °C tetracyclo[3 3 0 0^{2,4} 0^{3,6}]oct-7-ene is converted into equilibrating dihydropentalenes within 1—2 s

Tetracyclo[3 3 0 0^{2,4} 0^{3,6}]oct-7-ene (**1**)[1] provides a novel entry into the $(CH)_8$ energy surface,[2] it is related to the little known (**2**) and also the diradical (**3**), which has been invoked in several $(CH)_8$ interconversions [3]



(1)



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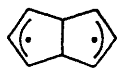

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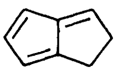

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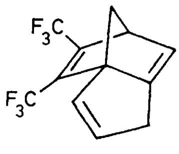

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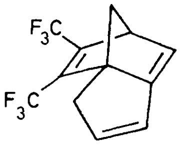

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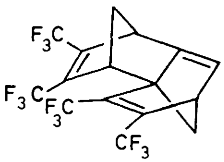

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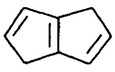

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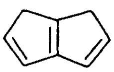

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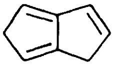

(10)

Thermolysis of (**1**) in a flow system (N_2, 2 Torr, *ca* 1 s) gives a mixture of products which are subject to rapid polymerization and isomerization upon g l c Catalytic hydrogenation of this mixture yielded *cis*-bicyclo[3 3 0]-octane as the only product By trapping the thermolysis mixture with excess of hexafluorobut-2-yne (HBF) four compounds were obtained,† which from mass, ^{1}H n m r , and u v spectra were identified as the dihydropentalene (**4**),[4] the two HBF–C_8H_8 adducts (**5**)‡ and (**6**)§ and an $(HBF)_2$–C_8H_8 adduct whose structure is most probably (**7**) ¶ The adducts (**5**), (**6**), and (**7**) are derived from the isomeric dihydropentalenes (**8**), (**9**), and (**10**),[5] respectively The variation in product composition with temperature is shown in the Figure The dihydropentalenes (**4**), (**8**), (**9**), and (**10**) interconvert under the conditions of their formation Tetracyclo[3 3 0 0^{2,4} 0^{3,6}]octane is stable upon flow pyrolysis up to 400 °C at which temperature (**1**) is completely converted into the products This shows that the double bond in (**1**) is essential for the ease of the rearrangement Two mechanisms are clearly compatible with this finding (A) Intramolecular reverse Diels–Alder reaction of (**1**) yielding the dihydrocalicene (**2**) After a [1,5] H shift, (**2**) can give the observed products by a vinylcyclopropene–cyclopentadiene rearrangement (B) Homolysis of the C(1)–C(2) bond in (**1**) followed by fission of the C(3)–C(4) bond This leads to the bicyclo[3 3 0]octadienyl diradical (**3**), which has been postulated as a precursor of (**10**) in the thermolysis of cyclo-octatetraene at high temperatures [6] Possibility (A) is preferred because (**3**) has also been invoked in the formation of other products,[3] which were not found in the thermolysis of (**1**), although they were proved to be stable under the reaction conditions

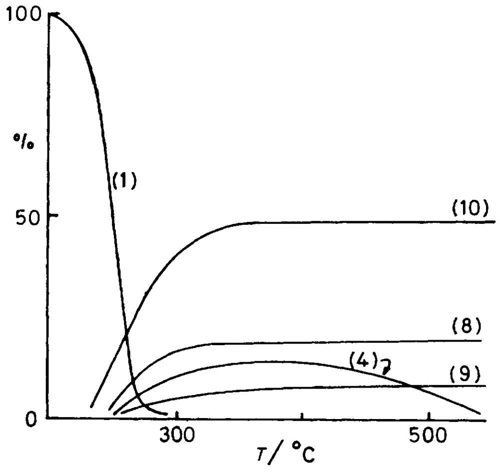

Figure Composition (%) of the mixtures obtained from the thermolysis of (**1**) at various temperatures

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† Isolated by preparative g l c [3 8% SE-30, 83 °C, relative retention times (r r t) (**4**) 0 26, (**5**) 0 39, (**6**) 0 44, and (**7**) 1 00, 10% Carbowax 20 M, 98 °C, r r t (**5**) 0 81 and (**6**) 1 00]

‡ ^{1}H N m r (90 MHz), δ (Me_4Si, $CDCl_3$) 2 03br (1H, d, *J* 6 5 Hz), 2 48 (1H, dd, *J* 6 5 and 1 8 Hz) 3 06 (2H, m), 4 04br (1H, s), and 6·20 (3H, m), u v (cyclohexane), λ_{max} 251 nm (sh, ϵ 125)

§ ^{1}H N m r (90 MHz), δ (Me_4Si, $CDCl_3$) 1 87br (1H, d, *J* 6 8 Hz), 2 34 (1H, dd, *J* 6 7 and 1 5 Hz), 2 55br (1H, d, *J* 19 3 Hz), 3 09br (1H, d, *J* 19 3 Hz), 4 14br (1H, s), 6 17br (1H, dd, *J* 3 2 and 1 0 Hz), and 6 44br (2H, s), u v (cyclohexane), λ_{max} 211 (ϵ 12600), 243 (6400), and 280 nm (sh, 1600)

¶ ^{1}H N m r (90 MHz), δ (Me_4Si, $CDCl_3$) 1 86br (1H, d, *J* 7 0 Hz), 2 24br (1H, d, *J* 10 3 Hz), 2 39br (1H, d, *J* 7 0 Hz), 2 56br (1H, d, *J* 10 3 Hz), 3 81br (1H, s), 3 90br (2H, s), and 6 43br (1H, d, *J* 3 0 Hz), u v (cyclohexane), λ_{max} 208 (ϵ 2600) and 242 nm (sh, 500) employed by us. We are presently studying the thermolyses of derivatives of (**1**) in order to clarify this point.

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