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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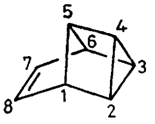
Summary At 270—500 °C tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene is converted into equilibrating dihydropentalenes within 1—2 s.

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]



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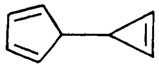

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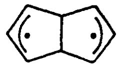

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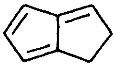

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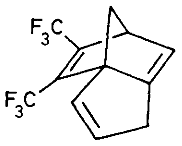

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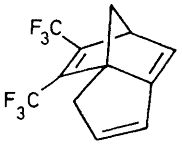

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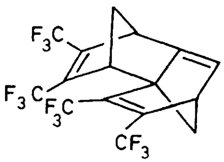

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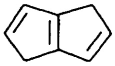

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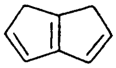

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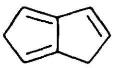

(10)

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$_8$H$_8$ adducts (**5**)[‡] and (**6**)[§] and an (HBF)$_2$–C$_8$H$_8$ 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

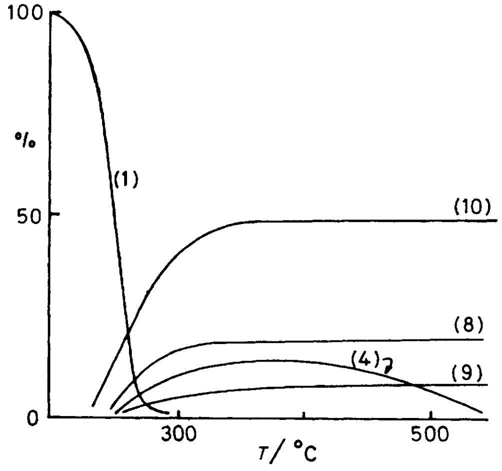

Figure Composition (%) of the mixtures obtained from the thermolysis of (**1**) at various temperatures.

[†] 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$_4$Si, 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$_4$Si, 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$_4$Si, 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.

Part of this work has been carried out with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) *via* the Netherlands Foundation for Chemical Research (S.O.N.). We thank Professor Hafner for the spectra of (**4**).

(*Received*, 17*th March* 1980, *Com.* 285.)

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