

## [CH]<sub>12</sub> Hydrocarbons. Directed Synthesis of Pentacyclo[6,4,0<sup>6,11</sup>,0<sup>7,9</sup>,0<sup>10,12</sup>]-dodeca-2,4-diene<sup>1</sup>

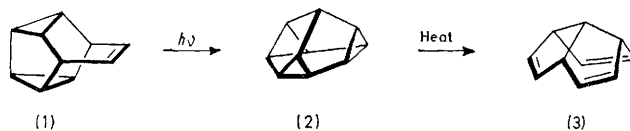
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*Summary* Synthesis of pentacyclo[6,4,0<sup>6,11</sup>,0<sup>7,9</sup>,0<sup>10,12</sup>]-dodeca-2,4-diene has been achieved in four steps through directed bond reorganization of tetracyclo[5,3,2,0<sup>2,5</sup>,0<sup>6,8</sup>]-dodeca-3,9,11-triene (**4**).

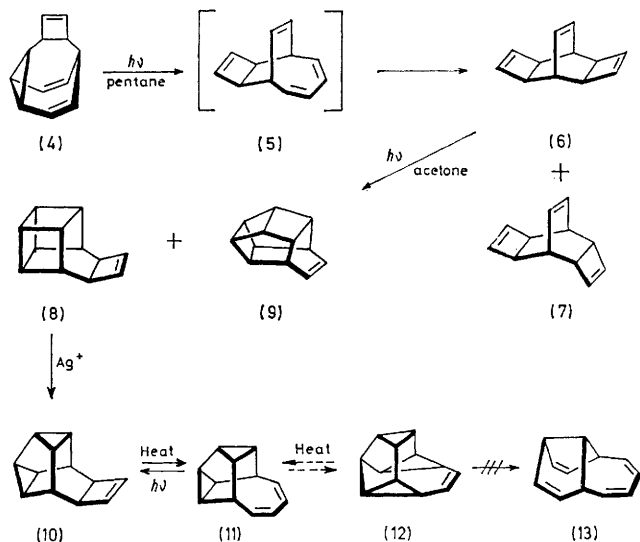
THE strained [CH]<sub>10</sub> hydrocarbon snoutene (**1**)<sup>2</sup> is of interest because it undergoes a highly specific degenerate thermal rearrangement<sup>2</sup> and is transformed readily upon direct irradiation to diademane (**2**), an immediate precursor of the triquinacene system (**3**).<sup>3</sup> The unusual structural features in (**1**) which provide the molecule with such an

exceptional capacity for bond reorganization prompted us to prepare the [CH]<sub>12</sub> homologue (**11**). Photolysis (450 W Hanovia medium-pressure arc) of dilute pentane solutions



of (**4**)<sup>4</sup> through quartz led within 2 h in greater than 80% yield to a mixture (ca. 50:50) of (**6**) and (**7**) whose identities

were established by direct comparison with authentic samples.<sup>5</sup> This conversion is envisaged as deriving from initial isomerization of (4) to (5) according to the generalized pathway elucidated by Katz and Cheung<sup>6</sup> and subsequent disrotatory cyclization of the newly formed 1,3-diene portion along both available stereochemical avenues. This last step has previously been investigated independently by Stowell with identical results.<sup>5</sup>



When the equimolar mixture of (6) and (7) was subjected to acetone-sensitized irradiation (200 W Hanovia lamp, Pyrex, 7 h), there was obtained after g.l.c. separation and purification a 20% yield of the cubyl hydrocarbon (8), a small quantity (2%) of the known<sup>7</sup> polycyclic (9), and traces of an as yet uncharacterized isomer. The structural assignment of (8) follows from analytical and m.s. data, its n.m.r. spectrum [ $\delta$  (CDCl<sub>3</sub>) 2.4—2.6 (2H, m), 2.6—2.85 (2H, m), 2.85—3.3 (6H, m), and 6.05 (2H, s)], and its vapour-phase fragmentation at 450° and 2 mm to a mixture of (6) (28%) and (7) (72%). The formation of (9) was unexpected. A hypothetical rearrangement scheme for

effecting the necessary face-to-face juxtaposition of the two cyclobutene rings would involve photoisomerization of (4) in the alternative stereochemical sense to give the *endo*-isomer of (5), cyclization of which gives (7) and minor quantities of *endo,endo*-tetracyclo[4,4,2,0<sup>2,5</sup>,0<sup>7,10</sup>]dodecatriene, followed by intramolecular (2 + 2) cycloaddition. Although the latter hydrocarbon was not detected in the mixture of (6) and (7), its presence in low concentration (<3%) may have gone undetected.

When treated with a solution of silver nitrate in methanol-water (4:1) at 25° for 3 h, (8) underwent quantitative isomerization<sup>8</sup> to (10) [ $\delta$  (CDCl<sub>3</sub>) 1.12—2.20 (6H, m, cyclopropyl), 2.3—2.65 (2H, m, bridgehead), 2.65—2.9 (2H, m, allylic), and 6.15 (2H, s, olefinic)]. This conversion follows the precedented<sup>9</sup> ( $\sigma_{2a} + \sigma_{2a}$ ) bond relocation process which simultaneously transmutes the set of four multiply fused cyclobutanes to pairs of three- and five-membered rings. Apparent in the n.m.r. spectrum of (10) is the absorption of area 6 due to the cyclopropyl hydrogens which appears at higher field than any of the protons in (8).

Although the hexacyclic hydrocarbon (10) is thermally stable, pyrolysis at 580° and 1.5 mm did result in partial conversion into (11). Sole operation of the disrotatory opening of the cyclobutene fraction was indicated by the electronic [ $\lambda_{max}$  (EtOH) 285 ( $\epsilon$  2570) and 295sh nm (2250)]<sup>10</sup> and n.m.r. spectra [ $\delta$  (CDCl<sub>3</sub>) 1.25—1.6 (2H, m, cyclopropyl), 1.85—2.15 (4H, m, cyclopropyl), 2.45—2.8 (2H, m, bridgehead), and 5.35—5.6 (4H, m, olefinic)] and by the efficient and rapid reconversion of (11) upon direct irradiation.

The excited-state behaviour of (11) appears to be restricted merely to diene ring closure. The thermal stability of (11) provides no information on its possible interconversion with (12), but suggests that if (12) does exist in equilibrium with (11) at elevated temperatures symmetry-allowed six-electron bond relocation returning (11) is substantially favoured over the forbidden reaction (8-electron process) which would afford (13).

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<sup>1</sup> For previous paper in the series see G. Zon and L. A. Paquette, submitted for publication to *J. Amer. Chem. Soc.*

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<sup>5</sup> L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, 1971, **93**, 5735; *Tetrahedron Letters*, 1959, 4159.

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<sup>10</sup> The  $\lambda_{max}$  values are seen to be shifted to longer wavelengths relative to those of bicyclo[4,2,2]deca-2,4,7,9-tetraene: M. Jones, jun., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, 1970, **92**, 3118.