

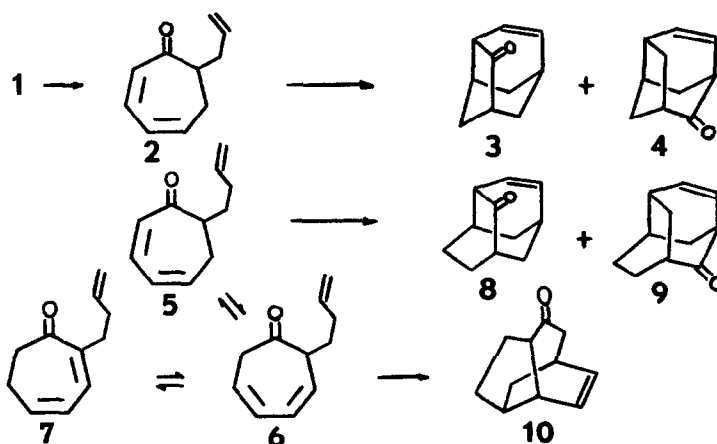
MULTIPLE THERMAL REARRANGEMENTS. IV. THE PYROLYSIS OF  
2-(4-PENTENYL)-DIHYDROTROPONE

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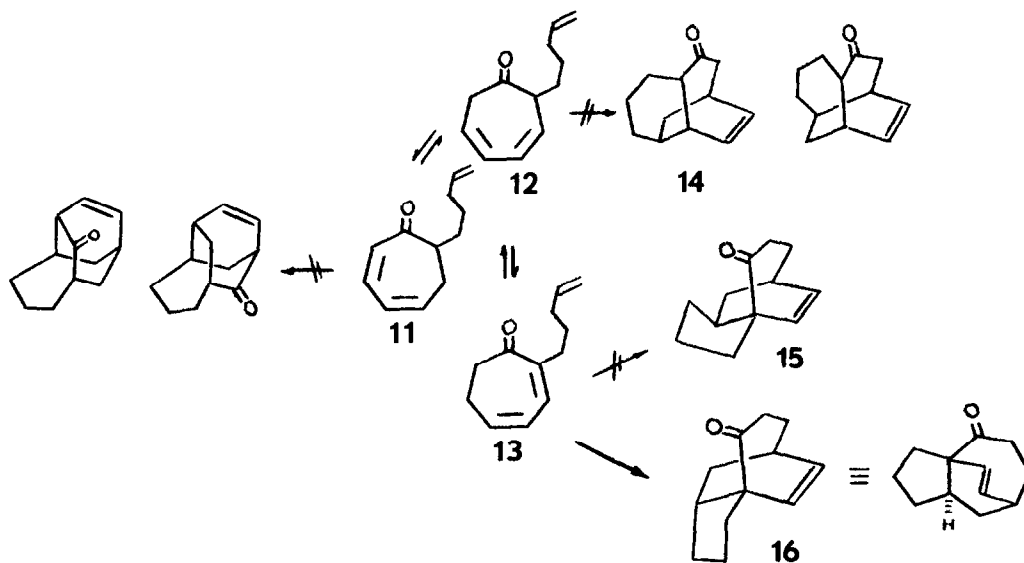
In previous studies we have shown that the thermal rearrangement of appropriately substituted cycloheptatrienes and dihydrotropone provides a facile synthetic entry to new bridged polycyclic systems. For example, pyrolysis of 7-allyloxycycloheptatriene (1) produces, in high yield, equal amounts of 2-protoadamantenone (3) and 10-protoadamantenone (4).<sup>1</sup> These tricyclics are  $[\pi^2_s + \pi^4_s]$  cycloaddition products derived from 2-allyl-2,3-dihydrotropone (2) which is gen-



erated under the reaction conditions by sequential sigmatropic reactions.<sup>2</sup> The thermal rearrangement of 2-(3-butenyl)dihydrotropone 5-7 gave three new bridged polycyclics 8, 9 and 10.<sup>3</sup> Here too the major  $[\pi^4s + \pi^2s]$  cycloaddition pathway proceeded through the 2-alkenyl-2,3-dihydrotropone (5). In this case, however, the reaction was further complicated by product derived from the 2-alkenyl-2,7-dihydrotropone (6).

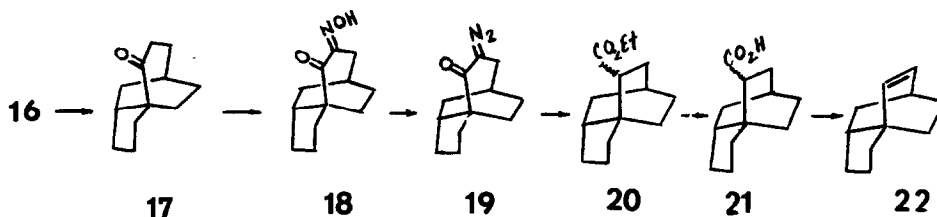
We now report that thermal rearrangement of the homologous system, namely the 2-(4-pentenyl) dihydrotropone, proceeds exclusively via a final cycloaddition pathway involving yet another isomeric dihydrotropone (a 7-alkenyl 2,3-dihydrotropone) and that the reaction, in marked contrast to the previous cases, proceeds with 100% constitutional and stereochemical selectivity to produce (16) in high yield.

Reaction of 4-pentenylmagnesium bromide<sup>4</sup> with tropone<sup>5</sup> at  $-78^\circ$  gave a mixture 2-(4-pentenyl) dihydrotropone 11-13 (63%, bp  $110-111^\circ$  (0.7 mm)). In theory, there are six tricyclic products which could be formed during thermal rearrangement of the dihydrotropone. Indeed, we had anticipated from our previous studies and examination of molecular models that 14, derived from the 2-(4-pentenyl)-2,7-dihydrotropone (12), might be a major component of the thermal rearrangement. Pyrolysis of the dihydrotropone at  $200-205^\circ$  (heptane, 24 hrs) gave only one tricyclic ketone in



77% yield which, by further studies outlined below, was shown to be endo-tricyclo [5.3.2.0<sup>1,5</sup>] dodec-11-en-10-one (16) (bp 70-72° (0.7 mm),  $\nu_{\max}^{\text{CCl}_4}$  1706, 1699, 1694  $\text{cm}^{-1}$ ).<sup>6,7</sup>

The key features of the nmr spectrum which gave an immediate clue to the structure of this rearrangement product were the resonances of the vinyl protons which appear as a triplet and doublet centered at  $\tau$ 3.75 and 4.40 respectively. The latter doublet was particularly revealing since this indicated that one bridgehead proton allylic to the carbon-carbon double bond was absent.<sup>8</sup> Only 15 and its epimer 16 fulfill this condition. Resolution of the latter ambiguity and further structure proof of 16 is based on its conversion to the known endo-tricyclo [5.2.2.0<sup>1,5</sup>]undec-8-ene (22).<sup>9</sup> Hydrogenation of 16 gave 17 (bp 126-127° (1.0 mm)  $\nu_{\max}^{\text{CCl}_4}$  1702, 1699, 1695  $\text{cm}^{-1}$ )<sup>10</sup> which was converted to 18 (mp 145.2-146.1°(dec)) with isoamyl nitrite.<sup>11</sup> Treatment of 18 with chloramine<sup>12</sup> gave the  $\alpha$ -diazoketone 19 which on photolysis in ethanol



gave the ring-contracted ester 20 which in turn was hydrolyzed to acid 21 (mp 112.0-113.2). Oxidative decarboxylation of 21 with lead tetraacetate-cupric acetate<sup>13</sup> gave olefin 22 which was identical (nmr and ir spectra) with an independently synthesized sample.<sup>9,14</sup>

We believe that 16 could find application in the synthesis of bi- and tricyclic sesquiterpenes having a hydro-azulene skeleton.

Studies concerned with the thermal behavior of other alkenyl and cycloalkenyl dihydroterpenes are in progress.

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4. M. Kharasch and C. Fuchs, *J. Org. Chem.*, **9**, 359 (1944).
5. P. Radlick, *ibid.*, **29**, 960 (1964).
6. Semicarbazone of 16, mp 213.0-213.9°.
7. Satisfactory elemental analyses were obtained for all new compounds with the exception of the  $\alpha$ -diazoketone 19 which was characterized by its I.R. spectrum.
8. Using the previously synthesized compounds as models, two "triplet" resonances for the vinyl protons would be anticipated for the tricyclic products derived from 11 and nearly equivalent vinyl proton resonances for 14.<sup>1,3</sup>
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14. We are grateful to Professor A. Krantz, State University of New York, Stony Brook, N.Y., for supplying spectra of 22.