

THERMAL TRANSFORMATIONS OF 1,2-CYCLONONADIENE

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Although thermal dimerizations and related cycloaddition reactions of allenes have received attention,² relatively little work has been reported on unimolecular thermal transformations of this class of compounds.³ This report is concerned with the thermal behavior of 1,2-cyclononadiene (1).

Pyrolysis of 1 in a flow system at 640° and 0.3 mm pressure resulted in 90% conversion to three products identified as 1-nonen-8-yne⁴ (2), cis-bicyclo[4.3.0]non-7-ene⁴ (3), and trans-bicyclo[4.3.0]non-2-ene⁴ (4) in the ratio of 65:23:12.

Compound 2 displays the spectral characteristics of terminal vinyl and acetylene groups [ir 3.03, 4.7, 6.08, 10.1, and 11.0 μ ; nmr δ 5.7 and 4.95 (m, 3, $\text{CH}=\text{CH}_2$), 2.12 (m, 4, $\text{C}=\text{CCH}_2$ and $\text{C}\equiv\text{CCH}_2$), 1.75 (t, 1, J = 2 Hz, $\text{C}\equiv\text{CH}$), and 1.41 (m, 6, CH_2)] and consumed three moles of hydrogen on catalytic hydrogenation producing n-nonane.

Compounds 3 and 4 are also isomeric with 1 as determined by mass spectrometry. Isomer 3 [ir 3.30 and 6.08 μ ; nmr δ 5.52 (s, 2, $\text{CH}=\text{CH}$)⁵ and 2.4 to 1.1 (m, 12)] was hydrogenated over platinum oxide to produce hydrindane (98% cis, 2% trans).^{6,7} Ozonolysis followed by peracetic acid work-up transformed 3 to cis-cyclohexane-1-carboxy-2-acetic acid (5), mp 145-146° (lit.⁸ 147°), which was converted to the cis-anhydride, mp 55-56° (lit.⁸ 57°). Additional evidence for the cis-ring juncture was obtained by equilibration of the dimethyl ester of 5 with sodium methoxide which effected 55% conversion to a new species, presumably the trans isomer.

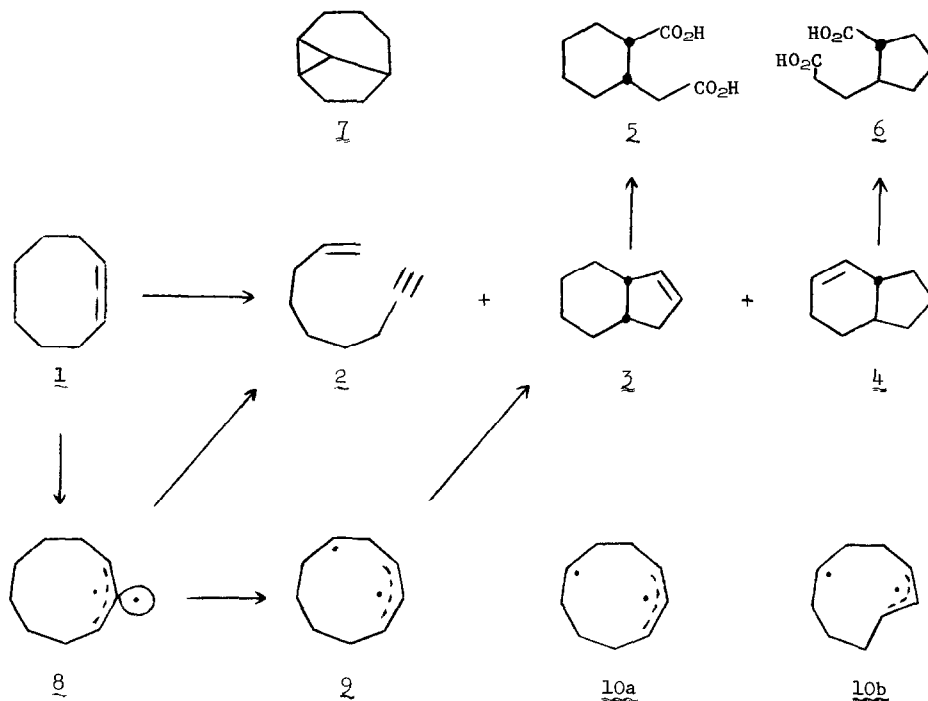
Hydrogenation of 4 [ir 3.30 and 6.1 μ ; nmr δ 5.60 (m, 2, $\text{CH}=\text{CH}$) and 2.25 to 0.9 (m, 12)] over platinum oxide produced hydrindane (94% trans, 6% cis), and ozonolysis gave trans-cyclopentane-1-carboxy-2-propionic acid (6), mp 100-101° (lit.⁹ 101.5°). The dimethyl ester of 6 was stable to sodium methoxide.

Several possible mechanistic pathways to the products were eliminated by examination of potential intermediates. Pyrolysis of tricyclo[6.1.0.0^{5,9}]nonane¹⁰ (7), the photoproduct from

1,¹¹ resulted in only 15% conversion to products under the reaction conditions. Therefore, the absence of 7 in the pyrolysate of 1 effectively rules it out as an intermediate. Samples of cis,cis-1,3- and cis,cis-1,4-cyclononadiene¹² were also subjected to the reaction conditions but led to products unlike those obtained from 1.

The conditions required to effect thermal conversion of 1 are relatively drastic, suggesting that high-energy intermediates may be involved. Acetylene 2 is formally the product of a retro-ene fragmentation.¹³ However, substantial molecular deformation is required to achieve the required cyclic geometry for concerted reaction, and an alternate route to product may obtain. An attractive speculation is that thermal activation gives a vibrationally excited planar allene 8 which can be viewed as two component radical units—a delocalized allylic system plus an orthogonal radical center on the middle allenic carbon. Hydrogen transfer from an appropriate methylene group to one end of the allylic radical with subsequent or simultaneous bond reorganization leads from 8 to acetylene 2 smoothly. Intermediate 8 can also be invoked to rationalize the formation of the bicyclic products. Thus, transannular hydrogen abstraction by the central allenic carbon via five- or six-center processes generates biradicals 9 and 10, respectively. Coupling of these species in the appropriate fashion gives 3 and 4. More complicated mechanistic possibilities exist, but detailed consideration of these is not profitable at the present time. Some support for the proposed capability of the middle allene carbon to abstract hydrogen is found in the recent work of Ward and Karafiath concerned with thermal and photochemical reactions of allenes.¹⁴

Two features concerning the production of 3 and 4 deserve special comment. First, the observed 2:1 ratio of 3:4 requires a preference for 1,4- over 1,5-hydrogen transfer (assuming the above mechanistic description). The reason for this unusual situation remains obscure. The second point concerns the high selectivity in the ring juncture stereochemistry which is opposite in the two cases. Assuming a planar allylic radical, models of 9 indicate that 3 should be formed with a cis stereochemistry regardless of the allylic radical stereochemistry. On the other hand, models of 10 suggest that the cis,cis isomer 10a should give cis product, whereas the cis,trans isomer 10b favors the observed trans stereochemistry of 4. The preference for reaction through 10b could be the results of destabilization of 10a because of non-bonded interactions between the alkyl substituents, a feature which is presumably important in the transition state for ring closure from 10a.



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5. The small coupling between olefinic and adjacent allylic protons is characteristic of cyclopentenes: Nmr Sadtler Standard Spectra, number 5162.
6. Hydrogenation of **3** and **4** over 10% palladium-on-carbon resulted in the formation of 4,5,6,7-tetrahydroindane.

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