

THE SYNTHESIS AND THERMAL REARRANGEMENT OF  
CIS-9-METHYLENEBICYCLO[6·1·0]NONENE DERIVATIVES

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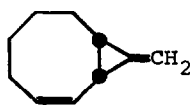
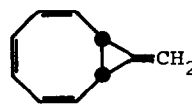
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While the chemistry of methylene cyclopropane appears well documented,<sup>3</sup> to the best of our knowledge there are no reported attempts to fuse this small ring system to a medium size carbocycle. We wish to report here the attempted preparation of two examples (1,2) of this unique fusion and, due to their thermal instability, the resultant formation of two additional interesting ring systems.

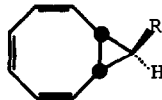
The entry into the cis-9-methylenebicyclo[6·1·0]nonene system was accomplished via Cope eliminations of the amine oxides 6 and 10. In each case the unsaturated amine oxide was ultimately obtained from the acid chlorides 3 and 7<sup>4</sup>. This transformation was accomplished by conversion of 3 and 7 to the amides 4 and 8 with anhydrous dimethyl amine in ether, reduction of the amides to the amines with lithium aluminum hydride, and oxidation of the amines to the amine oxides with 30% hydrogen peroxide in methanol. The Cope eliminations of 6 and 10 were then conducted by heating the syrupy amine oxide at 130-160°C/0.1 mm in a vacuum distillation apparatus and collecting the volatile products in a cooled receiver. The pure hydrocarbons were then isolated by pentane extraction and fractional distillation or preparative chromatography.

When the hydrated amine oxide 6 was heated to 150° it rapidly lost the elements of water and dimethyl hydroxylamine and resulted in the formation (50%) not of the expected methylene cyclopropane 1 but of 3-methylene-1,4-cyclonadiene, 11. Examination of the acid soluble fraction showed it to contain O-(cis-bicyclo[6·1·0]nona-2-ene-9-carbinyl)-N,N-dimethyl hydroxylamine (20%), the result of alkyl to oxygen migration in 6. The structure of 11 is supported by its ultraviolet absorption ( $\lambda_{\max}$  250 m $\mu$ ,  $\epsilon$  = 8200), its infrared adsorption at 11.3 $\mu$ , and by its nmr spectrum ( $\tau$ 3.89 doublet

(2H),  $\tau$ 4.46 doublet triplet (2H),  $\tau$ 5.10 singlet (2H),  $\tau$  7.60 multiplet (4H) and  $\tau$ 8.33 multiplet (4H)). Hydrogenation of 11 with platinum in ether led exclusively to methylcyclononane<sup>5</sup>. The facile conversion of 1 and 11 is not surprising in view of the known rearrangement of cis-bicyclo[6.1.0]nona-2-ene to cis,cis-1,4-cyclononadiene via a [1,5] sigmatropic rearrangement of

12R

- 3 COCl  
4 CON(CH<sub>3</sub>)<sub>2</sub>  
5 CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>  
6 CH<sub>2</sub>NO(CH<sub>3</sub>)<sub>2</sub>

R

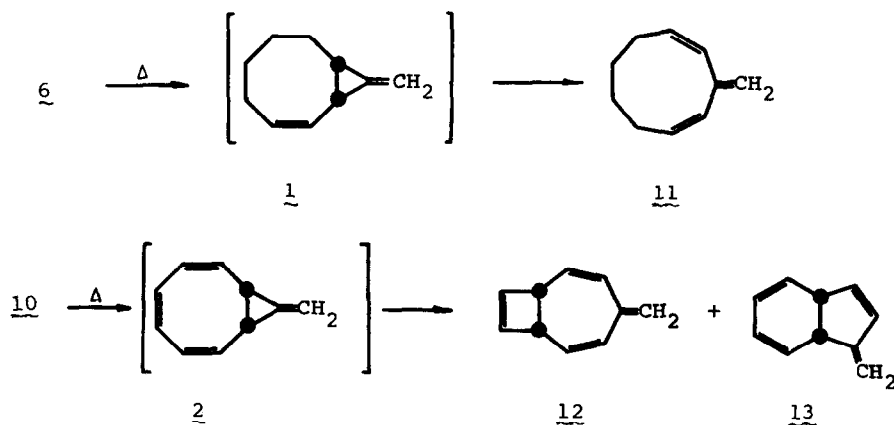
- 7 COCl  
8 CON(CH<sub>3</sub>)<sub>2</sub>  
9 CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>  
10 CH<sub>2</sub>NO(CH<sub>3</sub>)<sub>2</sub>

hydrogen<sup>6</sup>. The high strain energy associated with a methylene cyclopropane ring would be expected to accelerate this process.

Decomposition of the amine oxide 10 resulted in the formation of a 2:3<sup>7</sup> mixture of the sensitive olefins 12 and 13<sup>8</sup> (52%). Inspection of the acid soluble fraction showed the presence of 3% of the alkyl to oxygen migration product of 10. Separation of 12 and 13 was accomplished by column chromatography on 12.5% silver nitrate on silica gel, eluting with pentane. The structure of 12 was confirmed by its infrared absorption at 1558 and 3132 cm<sup>-1</sup> for the cyclobutene ring<sup>9</sup> and by its nmr spectrum with two cyclobutene protons at  $\tau$ 3.97(s), two vinyl protons, C<sub>3</sub>C<sub>5</sub>, at  $\tau$ 4.05 (d, J = 14Hz), two vinyl protons, C<sub>2</sub>C<sub>6</sub>, at  $\tau$ 4.48 (dd, J<sub>1,2</sub>=4.5Hz), two exocyclic methylene protons at  $\tau$ 4.95(s) and the two bridge protons at  $\tau$ 6.28 (d, J<sub>1,2</sub>=4.5Hz). The structure of 13 as cis-3-methylene-8,9-dihydroindene was confirmed by its acid catalyzed rearrangement to 1-methylindene in methanol and by catalytic hydrogenation to the epimeric cis-methylhydrindanes<sup>5</sup>.

The possibility that rearrangement of 6 and 10 had occurred prior to

elimination was discounted since when 10 was heated to just below its decomposition point, no rearrangement was observed<sup>10</sup>. In addition, if rearrangement occurred before elimination, some rearranged oxygen migration product should have been observed.



The conversion of 2 to 12 is easily understood as occurring via a [3.3] sigmatropic migration (Cope rearrangement) and is well documented for cis-divinyl cyclopropanes<sup>11</sup>.

The question, of whether 12 is an intermediate in the conversion of 2 to 13 and if bicyclo[5.2.0]nonatriene is involved as a general intermediate in the bicyclo[6.1.0]nonatriene to 8,9-dihydroindene rearrangement,<sup>5,12</sup> we hope to answer in the near future.<sup>13</sup>

#### References

1. Alfred P. Sloan Fellow
2. Present Address; Shell Development Company, Emeryville, California 94608
3. B. C. Anderson, J. Org. Chem., 26, 2573 (1961) and references cited therein.
4. M. Jones, Jr., L. T. Scott, J. Am. Chem. Soc., 89, 150 (1967).
5. P. Radlick, W. Fenical, ibid., 91, 1560 (1969).
6. D. Glass, R. Boikess, S. Winstein, Tetrahedron Letters, 999, (1966).
7. The ratio of 12 to 13 was found dependent upon decomposition time. When the elimination was conducted very slowly only 20% 12 was formed.

8. Both 12 and 13 were very prone to polymerize, even at 0° and under nitrogen 12 can only be stored for 1-2 days.
9. P. Radlick, W. Fenical, Tetrahedron Letters, 4901, (1967).
10. To check the proposal that methylene cyclopropanes were being initially formed, the saturated amine oxide was prepared and decomposed. The elimination proceeded smoothly and cis-9-methylenebicyclo[6.1.0]nonane was formed (25%). The structure of this material was confirmed by hydrogenation to cis,syn-9-methylbicyclo[6.1.0]nonane.<sup>5</sup>
11. H. M. Frey, "Advances in Physical Organic Chemistry", Vol. 4, V. Gold, ed. Academic Press, New York, N.Y., 1966, pp. 163.
12. S. W. Staley, T. J. Henry, J. Am. Chem. Soc., 91, 1239, 7787, (1969).
13. We are very grateful to the Petroleum Research Fund administered by the American Chemical Society for support of this work and to Badische Anilin and Soda-Fabrik for a generous gift of cyclooctatetraene.