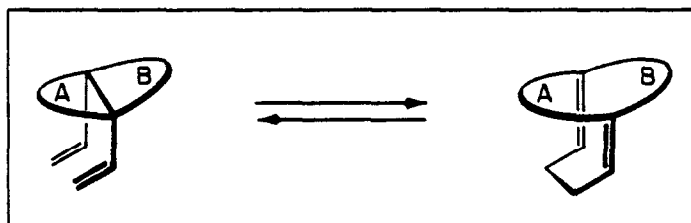


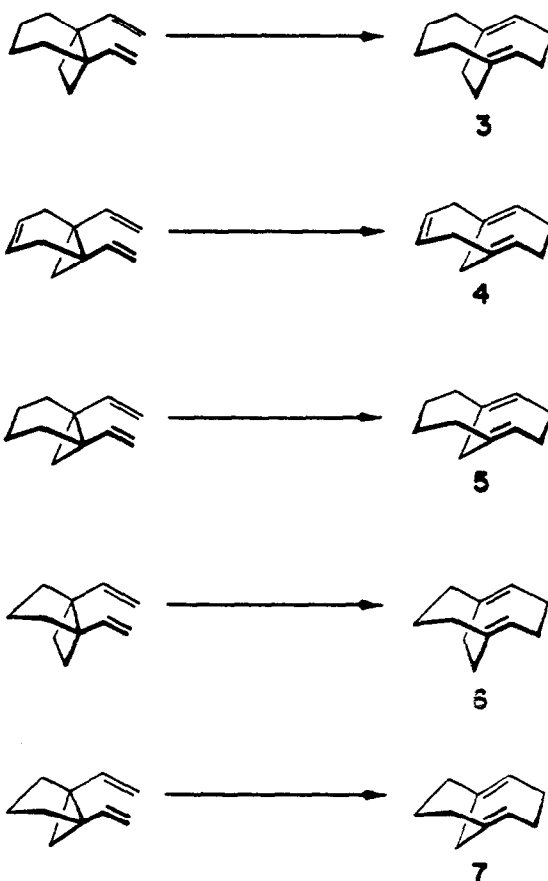
[3.3] Sigmatropic rearrangement of cis-1,2-divinylcycloalkanes can arise from two boat-like conformations.⁴ The endo conformation results in formation of a cis,cis-1,5-cyclooctadiene while rearrangement from the exo conformation produces a trans,trans-1,5-cyclooctadiene. In small and medium ring 1,5-cycloalkadienes the cis,cis-isomer is more stable;⁵ thermal rearrangement proceeds via the endo conformation.

If cis-divinyl groups occupy the bridgehead positions of bicyclo [n,m,o] alkanes, sigmatropic rearrangement will result in formation of a bicyclic trans,trans-1,5-cycloalkadiene, i.e. meso bridgehead diene 2. In the equation below the diene product is trans,trans in the B ring and cis,cis in the A ring. We anticipated that the trans,trans-1,5-diene component would be favored to reside in the largest ring. The overall position of equilibrium would dictate the success of the synthetic entry.

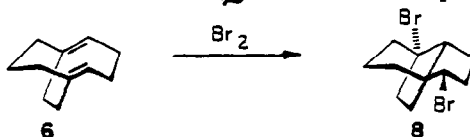


Synthesis of the required divinyl derivatives was accomplished by elaboration of the known bridgehead diesters.⁶ Thus LAH reduction followed by activated dimethylsulfoxide oxidation⁷ and bis Wittig olefination of the resulting dialdehydes affords good yields of divinyl compound. In several cases the divinyl product could not be isolated, rather spontaneous rearrangement to the bridgehead diene took place.⁸

The results are summarized in the Table. Several general trends can be made from these observations. In all cases, the equilibrium lies completely to the side of the bridgehead diene. Furthermore, a rough correlation exists between the strain energy of the bicyclic precursor and the rate of [3.3] sigmatropic rearrangement. For example, the lifetime of 1,4-divinylbicyclo [3.1.0]hexane (SE 33.5 kcal/mol) is short (minutes at 0°C) while 1,6-divinylbicyclo[4.1.0]heptane (SE 29.6 kcal/mol) has a half-life of 30 min at 25°C.



The proximate relationship of the two bridgehead double bonds is expected to manifest itself in the chemical behavior of these compounds. Preliminary results suggest this is so, for example, treatment of bridgehead diene 6 with Br_2 results in the uptake of one equivalent with formation of a single isomeric dibromide. The spectral properties of the adduct are consistent with the asymmetric dibromide (8) shown in the equation.⁹



We are continuing our investigation of the chemical and spectroscopic properties of these molecules as well as the synthesis of more highly strained members of this series.

Acknowledgment

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References and Footnotes

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3. K.J. Shea and S. Wise, Tetrahedron Lett., **1978**, 2283.
4. Rearrangement via the chair conformation gives rise to cis,trans-1,5-cycloalkadienes. In medium sized rings this configuration is at substantially higher energy than either cis,cis or trans,trans isomers. See for example E. Vogel and W. Grimme, Angew. Chem. Int. Ed. Eng., **1963**, 2, 739.
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6. (a) 1,5-dicarbomethoxybicyclo[3.1.0]hexane, R.N. McDonald and R.R. Reitz, J. Org. Chem., **1972**, 37, 2418; (b) 1,6-dicarbomethoxybicyclo [4.1.0]heptane, S.R. Wilson and R.B. Turner, J. Org. Chem., **1973**, 38, 2970; (c) 1,5-dicarbomethoxybicyclo[3.2.0] heptane and 1,6-dicarbomethoxybicyclo[4.2.0]octane, D.C. Owsley and J.J. Bloomfield, J. Org. Chem., **1971**, 36, 3768.
7. A.J. Mancuso and D. Swern, Synthesis, **1981**, 165.
8. All bridgehead dienes exhibit spectroscopic data consistent with the assigned structures;
 - 3 ¹H NMR (250 MHz, CDCl₃) δ 5.25 (m, 2H), 2.66, 2.53 (AB, J=3.1 Hz, 2H), 2.30 (m, 2H), 2.2-1.82 (m, 8H), 1.80-1.56 (m, 2H), 1.55-1.20 (m, 2H); ¹³C NMR (62.9 MHz, CDCl₃) δ 143.1 (bridgehead), 124.6, 40.3, 31.0, 28.6, 26.6; mass spectrum, m/e (CI) 163 (M+1);
 - 4 ¹H NMR (250 MHz, CDCl₃) δ 5.64 (m, 2H), 4.90 (m, 2H), 3.3 (d, J=3 Hz, 1H), 3.1-2.4 (m, 6H), 2.10 (m, contains d, J=13 Hz, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ 144.4, 126.5, 117.7, 38.5, 34.5, 25.5; mass spectrum, m/e (EI, 70 eV), 146 (M+).
 - 5 ¹H NMR (80 MHz, CDCl₃) δ 5.75 (m, 2H), 3.16 (d, J=12 Hz, 1H), 3.0-1.5 (m, 13H); ¹³C NMR (62.9 MHz, CDCl₃) δ 147.7, 118.2, 36.8, 32.3, 27.4, 25.4; mass spectrum, m/e (EI, 70 eV) 148 (M+).
 - 6 ¹H NMR (250 MHz, CDCl₃) δ 5.15 (m, 2H), 2.7-1.1 (m, 14H), ¹³C NMR (62.9 MHz, CDCl₃) δ 144.3, 125.2, 98.6, 38.3, 29.6, 28.0, 25.0; mass spectrum m/e (CI) 149 (MH+).
 - 7 ¹H NMR (250 MHz, CDCl₃) δ 4.63 (m, 2H), 2.90, 1.90 (AB, J=10 Hz, 2H), 2.60-2.00 (m, 10H); ¹³C NMR (62.9 MHz, CDCl₃) 155.4, 114.0, 41.5, 40.9, 37.7, 24.4; mass spectrum m/e (CI) 135 (MH+); UV (cyclohexane) 251 nm.
9. A similar finding has been reported for the bromination of tricyclo[4.2.2.2.^{2,5}]dodeca-1,5-diene. M.G. Matturro, R.D. Adams, and K.B. Wiberg, J. Chem. Soc., Chem. Commun., **1981**, 878.

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