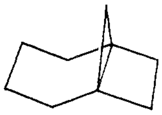
Communications

Reactions of a Highly Strained Propellane. Tetracyclo[4.2.1.1^{2,5}.0^{1,6}]decane[1]

Summary: The highly strained propellane 7 has been prepared and its reactivity toward thermal ring opening and addition of bromine, acetic acid, and dimethyl acetylenedicarboxylate are described.

Sir: Strained propellanes, **1-4**, are of interest because of the unusual hybridization of the central C-C bond, which approximates a p-p σ bond.[2] The rates of the thermal [2 + 2] ring opening reactions of **2-4** provide a quantitative test of predictions based on perturbation arguments.[2e] The syntheses and properties of propellane **1** and the [3.2.1] propellane **2** have been investigated,[2] and a carboxamide derivative of the [2.2.2] propellane has been recently synthesized.[2k,l] The highly strained [2.2.1] propellane, **4**, remains unknown.[2g] To mimic the geometry at the central bond of the [2.2.1] propellane **4** but keep the bond properties of **2** essentially unchanged with respect to perturbation arguments, we have prepared the tetracyclo[4.2.1.1^{2,5}.0^{1,6}]decane, **7**, and compared it to **1**, **2**, and **3** in its reactivity in addition reactions and thermal ring opening.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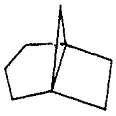
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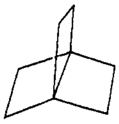
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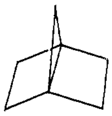
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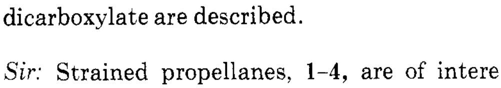
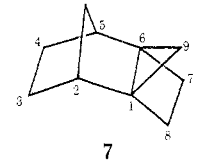
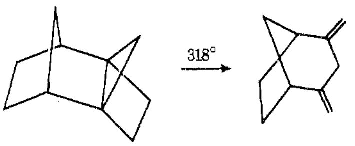


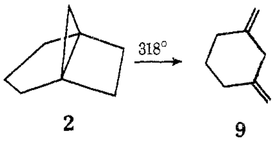


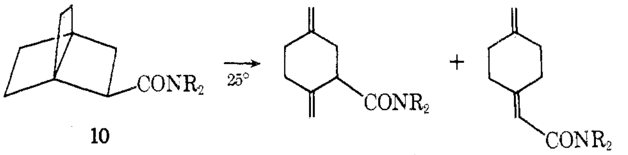
7

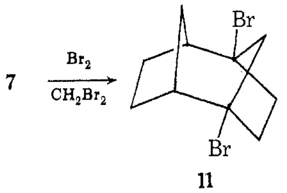
A degassed ethereal solution of Δ^{2,5}-tricyclo[4.2.1.0^{2,5}]nonene, **6**, prepared from **5**[3] was treated with cuprous bromide and gaseous diazomethane (175% excess) over 2.5 hr at 0° [4] to give **7** in 87% yield: bp 74-75° (13 mm); nmr (100 MHz) (CCl$_4$) δ 0.46 (d, *anti*-cyclopropyl H$_9$, 1 H), 0.71 (dt, anti H$_{10}$, 1 H), 0.92 (m, *syn*-cyclopropyl H$_9$, 1 H), 1.03 (m, syn H$_{10}$, 1 H), 1.34 (m, exo H$_7$, 2 H), 1.41 (m, exo H$_3$, 2 H), 1.90 (m, endo H$_3$, 2 H), 2.13 (m, endo H$_8$, 2 H), 2.37 (dt, bridgehead H$_2$, 2 H). Thus the endo protons on carbons 3, 4, 7, and 8 are deshielded by ~0.8 ppm because of steric compression,[5] and the syn protons on carbons 9 and 10 show a steric deshielding of ~0.5 ppm. The ir spectrum of **7** shows C-H stretching bands at 3045 cm^{-1} for sterically compressed hydrogens as well as at 3060 cm^{-1} for the cyclopropyl hydrogens.[6]

The gas-phase thermolysis of **7** and the related tricyclo[4.2.1.0^{1,5}]octane, **2**, proceeds to give the dienes **8** and **9**,[7] respectively. The more strained propellane **7** undergoes ring opening about six times as fast as **2** at 318°. Both propellanes, however, undergo ring opening much more slowly (by a factor of ~10^9) than the [2.2.2] propellane **10** described by Eaton.[2k] These results dramatically confirm the prediction made by Stohrer and Hoffmann,[2e] on the basis of perturbation theory, that the thermal ring opening of the [2.2.2] propellane should be faster than that of the [3.2.1] propellane.



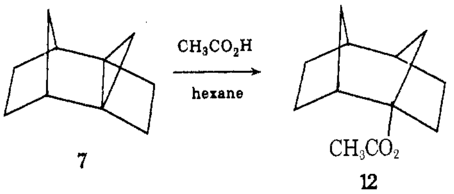




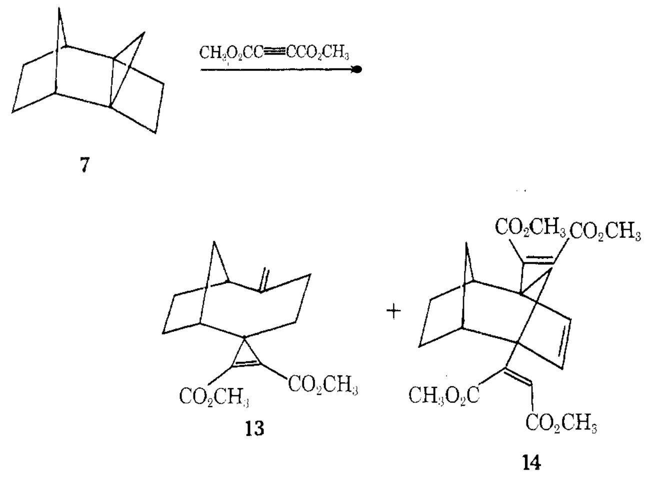


The reaction of **7** with bromine in dibromomethane is rapid at −50° and gives the dibromide **11**. The buttressing hydrogens in **11** show downfield shifts in the nmr of ~0.7 ppm for the endo protons and 0.8 and 1.5 ppm for the syn protons on carbons 9 and 10, respectively.

The rates of acetic acid addition to **2** and **7** have been measured in 0.60 *M* hexane at 25.6°. Although the central bond in **7** is expected to be significantly more strained than in **2**,[8] it is only ~1.5 times as reactive as **2** toward acetic acid. Surprisingly, the acetic acid addition to **7** is ~10 kcal/mol less exothermic[9] than to **2**. From comparison of the steric crowding shifts in the nmr spectra of **11** and **7**, there appears to be more steric compression at the syn hydrogens of C$_9$ and C$_{10}$ in **11** than in **7**.[10] This extra steric strain[11] in **12** could account for the difference in the exothermicities of acetic acid addition. In spite of the fact that acetic acid adds less exothermically to **7** than to **2**, the reactivity of the central σ bond in **7** is nevertheless greater than in **2** toward acetic acid. The half-life of **7** extrapolated to pure acetic acid is ~1 sec at 25° while the half-life is 1.6 hr for the [4.2.1] propellane **1**.[2j] This corresponds to a rate acceleration of ~10^4 as a result of the increase in strain from **1** to **2** or **7**.



The propellanes **7** and **2** react rapidly with dimethylacetylenedicarboxylate (DMAD) at 25° to give two unusual types of products.[12,13] Products **13** and **14** (and **15** and **16**) are formed in 80-90% yields. In carbon tetrachloride (1 *M*



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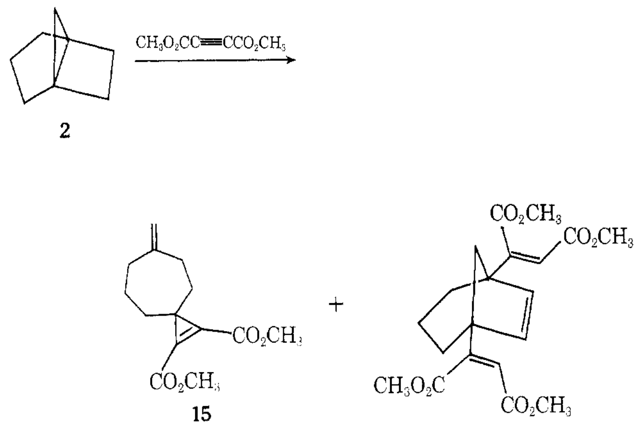
14



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15

16

DMAD) the ratio of **13** to **14** is 3:2, but the less strained propellane **2** gives less of the cyclopropene product. The ratio of **15** to **16** in carbon tetrachloride (1 *M* DMAD) is 1:7. The ratio of **13** to **14** increases with increasing solvent polarity, but is not sensitive to changes in the concentration of DMAD. Thus a simple mechanism based on partitioning of a 1:1 intermediate diradical between **13** and **14** can be eliminated. Investigation of other mechanistic possibilities is underway.

Supplementary Material Available. Full nmr data for compounds **7**, **8**, **11**, **12**, **13**, **14**, **15** and **16** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-2315.

References and Notes

(1) Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(3) D. H. Aue and R. N. Reynolds, *J. Amer. Chem. Soc.*, **95**, 2027 (1973).

(4) By the method of R. E. Pincock and J. I. Wells [*J. Org. Chem.*, **29**, 965 (1964)] and E. Müller and H. Kessler [*Tetrahedron Lett.*, 3037 (1968)].

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(7) W. J. Bailey and J. Economy, *J. Org. Chem.*, **23**, 1002 (1958).

(8) The corresponding olefins appear to differ by at least 3–4 kcal/mol in strain energy (ref. 3).

(9) Preliminary results for **2** give $\Delta H^\circ = 42 \pm 2$ kcal/mol and for **7** ΔH° is ~30 kcal/mol: E. S. Lewis, K. H. Leavell, R. Kluttz, R. N. Reynolds, and D. H. Aue.

(10) See K. B. Wiberg, K. C. Bishop, III, and R. B. Davidson, *Tetrahedron Lett.*, 3169 (1973), for a discussion of cases where reactivity toward electrophiles does not always parallel the relief of strain energy.

(11) The strain energy of the ring system for **11** and **12** has been calculated to be ~40 kcal/mol: E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8005 (1973).

(12) The structures of these products are supported by characteristic spectral data. The position of the double bond in **14** was established by using *exo*-3,4-dideuterio-**7**.

(13) See P. G. Gassman, *Accounts Chem. Res.*, **4**, 128 (1971).

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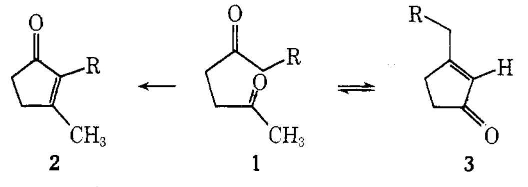
Cyclenones. V.[1] Mechanistic Factors in the Aldol Cyclization of 2,5-Alkanediones

Summary: The cyclization of 6-alkyl-2,5-hexanediones (**1**) in aqueous ethanolic base is a kinetically controlled reaction, with the major product being the 2-alkyl-3-methylcyclopent-2-enones (**2**).

Sir: The intramolecular aldol condensation is an important pathway for the synthesis of cyclenones. We have been studying those factors which influence the direction of cyclization of unsymmetrical diketones of the type $RCH_2CO(CH_2)_nCOCH_3$. In this, and in the accompanying communication, we wish to report the first definition of some of the kinetic *vs.* thermodynamic influences on the distribution of products for this reaction for the case $n = 2$.

In principle, alkaline treatment of systems such as **1** could give rise to tetrasubstituted[2] enones **2** or trisubstituted enones **3**. In practice, trisubstituted enones have not been reported[3] from such a reaction in the cyclopentenone[4] series. Reported failure to obtain products of general formula **3** can be explained by either of two hypotheses: (A) the tetrasubstituted enone **2** is the thermodynamically more stable cyclopentenone and that under the reaction conditions the formation of the trisubstituted product **3** is reversible; or (B) the reaction is kinetically controlled and compounds of type **3** are not formed at all under these conditions.



2 **1** **3**

The reported[5] isomerization of 3-ethylcyclohex-2-enone (**4**) to a 93:7 mixture of 2,3-dimethylcyclohexenone and **4**, by refluxing for 3 hr with 5% sodium hydroxide, lent some credence to hypothesis A.