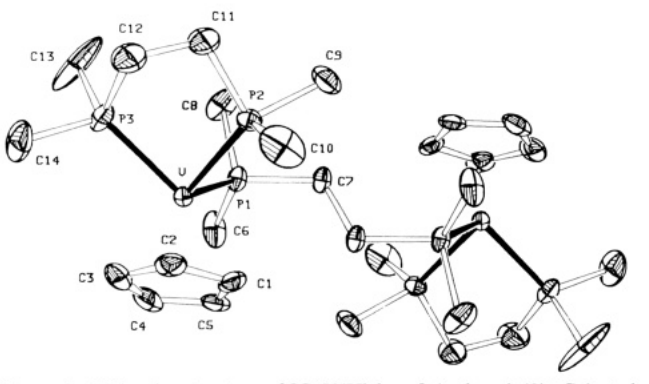

Figure 2. Molecular structure of $[CpV(H)dmpe]_2(\mu\text{-dmpe})$ (**2**). Selected structural parameters: V–P(1) = 2.369 (1) Å, V–P(2) = V–P(3) = 2.378 (1) Å, ∠P(1)–V–P(2) = 95.00 (4)°, ∠P(1)–V–P(3) = 117.40 (5)°, ∠P(2)–V–P(3) = 79.02 (4)°.

distance (which is too long for a triple bond, characteristically 2.2–2.4 Å[9]) and the diamagnetism of **1**. The V–H distances (1.64 (4) and 1.72 (4) Å) and the nonbonding separation of the H atoms of 2.01 (5) Å are similar to those found in $[CpV(\mu\text{-H})]_2(\mu\text{-}C_6H_6)$,[4] but the latter compound contains a puckered V_2H_2 ring with multiple metal–metal bond character (V–V = 2.425 (1) Å).

1 was isolated in 30% yield, but it is not the only product formed. From the mother liquor another compound can be obtained as orange-brown crystals from pentane or diethyl ether in 10–20% yield. This product is paramagnetic (by NMR), while the IR spectrum indicates the presence of a terminal hydride, with $\nu_{V-H} = 1560\ cm^{-1}$ ($\nu_{V-D} = 1105\ cm^{-1}$ in the D_2 reaction product, $\nu_{V-H}/\nu_{V-D} = 1.412$).

X-ray diffraction[10] revealed that the compound is the dimeric $[CpV(H)dmpe]_2(\mu\text{-dmpe})$ (**2**, Figure 2). Unfortunately, the positions of the hydride ligands could not be determined unequivocally from the Fourier difference map. However, a substantial asymmetry in the P–V–P angles can be seen (P(2)–V–P(3) = 79.02 (4)°, P(1)–V–P(2) = 95.00 (4)°, P(1)–V–P(3) = 117.40 (5)°), leaving room for the hydride ligand in the sector of the metal between P(1) and P(3).

As no metal–metal contacts are present in the structure, the vanadium atoms should behave like two isolated 17-electron low-spin ($S = 1/2$) d^3 centers. Indeed **2** is ESR active and in solution exhibits a complicated hyperfine splitting pattern with $g = 2.0003$. Replacing the hydride by a deuteride simplifies the solution ESR spectra considerably.[11] A comparison of these two ESR spectra indicates that the unpaired electron on each vanadium center in **2** interacts with one hydride ligand, $a(^1H) = 15.5$ G.[12] Simulation of the spectrum of **2**-d_2 confirmed additional interactions of the unpaired electron with the vanadium nucleus, $a(^{51}V) = 57.4$ G, and with three nonequivalent phosphorus nuclei, $a(^{31}P) = 30.5$, 33.5, and 36.0 G. The extensive delocalization of the unpaired electron, resultant in low spin-orbit coupling, is in accordance with the relatively large g value.

The mechanism of formation of **2** is unclear. Apparently, parallel with the reaction sequence in eq 1, some disproportionation occurs according to eq 2, where [CpVH] may be identified with the poorly soluble gray powder that is also observed in the reaction mixture.

$$33 + 3H_2 \rightarrow [CpV(H)dmpe]_2(\mu\text{-dmpe})\ (\mathbf{2}) + [CpVH]\downarrow + 3C_3H_8 \quad (2)$$

Once formed, the hydrido-bridged dimer **1** is fairly unreactive. For instance, it cannot be broken up into monomeric units by Lewis bases like THF or PMe_3. Pure **1** does not catalyze the hydrogenation and isomerization of 1-hexene at ambient conditions, whereas **3**, dissolved in 1-hexene under 1 atm of H_2, does.[6] Apparently it is necessary to trap the monomeric hydrido species immediately after hydrogenolysis of the V–C bond.

Acknowledgment. We thank Prof. K. G. Caulton for stimulating discussions and H. J. Heeres for practical assistance. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. 1, 111635-25-7; **2**, 111717-72-7; **3**, 110174-52-2; 1-hexene, 592-41-6.

Supplementary Material Available: Observed and calculated ESR spectra of **2**-d_2, tables of crystallographic data and positional and thermal parameters, and lists of interatomic distances and angles for **1** and **2** (13 pages); listings of observed and calculated structure factors for **1** and **2** (24 pages). Ordering information is given on any current masthead page.

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(9) (a) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886. (b) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982.

(10) **2** crystallizes in the monoclinic space group $P2_1/n$, $a = 8.429$ (2) Å, $b = 24.053$ (4) Å, $c = 9.468$ (5) Å, $\beta = 110.16$ (4)° (130 K), $Z = 2$. Reflections (2548) with $1° \leq \theta \leq 26°$ were considered observed. Nonmetal bound hydrogen atoms were located from the Fourier difference map and constrained at 0.95 Å from their corresponding carbon atoms in the final refinement cycles with use of isotropic fixed thermal parameters: $R = 0.042$, $R_w = 0.055$ ($w = 1$).

(11) In general $a(^2H)$ is 1–2 G, which remains unresolved in the spectrum.

(12) The only $a(^1H)$ observed so far in a vanadium system is 14.6 G in the reaction mixture of Cp_2V with $HSnEt_3$: Razuvaev, G. A.; Abakumov, G. A.; Gladyshev, E. N.; Fokeev, A. P.; Cherkasov, V. S. *Dokl. Akad. Nauk SSSR* **1982**, *266*, 135.

Stereochemistry of the Thermal Isomerization of Bicyclo[3.2.0]hept-2-ene to Bicyclo[2.2.1]hept-2-ene

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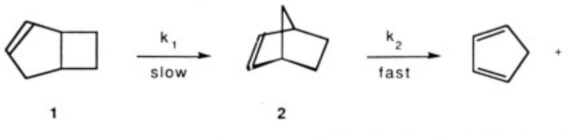
Sigmatropic [1,3] CHD-carbon migrations of unsubstituted bicyclic hydrocarbons constrained to isomerize suprafacially may provide stereochemical information sensitive to reaction mechanistic course and dynamics. Totally stereoselective inversion is consistent with an allowed, orbital symmetry controlled process,[1] while participation of both inversion and retention modes implicates competitive paths,[2] either parallel concerted processes with opposite stereochemistry[3] or the partitioning of a short-lived biradical intermediate. To know the stereochemical features of CHD-carbon shifts as a function of bicyclic system could provide grounds for distinguishing among these subtle but mechanistically significant alternatives.

Such stereochemical information has been gained for only one system: bicyclo[2.1.1]hex-2-ene labeled with deuterium at C5 gives 6-deuteriobicyclo[3.1.0]hex-2-ene with high but not complete stereoselectivity favoring inversion. At 197 °C in isooctane solution the retention component is 6.9%.[2]

We have followed the stereochemical course of the bicyclo[3.2.0]hept-2-ene (**1**) to bicyclo[2.2.1]hept-2-ene (**2**) isomerization.[4] Stereochemical assessment of this isomerization is experimentally challenging since the product **2** reacts further to give cyclopentadiene and ethene. At 276 °C, the maximum concentration of **2** to be expected is only 1–2%![4,5]



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(1) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511–2513. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim/Bergs., 1971.

(2) Newman-Evans, R. H.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 7994–7995. For the stereochemical aspects of the isomerizations shown by the isomeric 5-methylbicyclo[2.1.1]hex-2-enes, see: Roth, W. R.; Friedrich, A. *Tetrahedron Lett.* **1969**, 2607–2610.

(3) Berson, J. A.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 8917–8918. Fernandez, A. *J. Chem. Phys.* **1985**, *82*, 3123–3126.

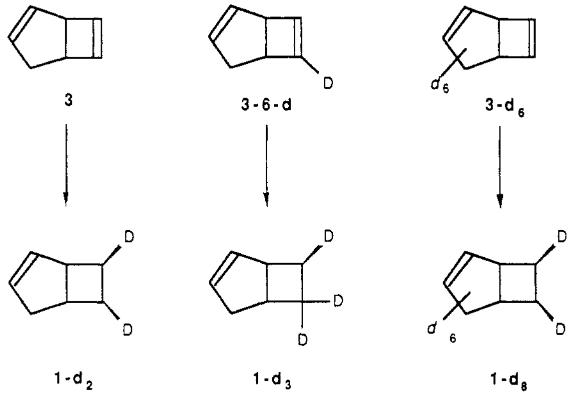
(4) Cocks, A. T.; Frey, H. M. *J. Chem. Soc. A* **1971**, 2564–2566.

Table I. Stereochemistry of [1,3] Carbon Shifts in Isomerizations of Deuteriated Bicyclo[3.2.0]hept-2-enes to Bicyclo[2.2.1]hept-2-enes

reactant[a] **1**-d_i	product **2**-d_i (C5,6)H exo/endo	NMR solvent	[1,3] shift retntn (%)
1-d_0	1.02	CD_3OD	
1-d_2	1.34	$CDCl_3$	21
	1.48	CD_3OD[b]	28
1-d_3	0.57	$CDCl_3$	27
	0.43	CD_3OD	18
	0.51	CD_3OD	23
	0.54	CD_3OD	25
1-d_8	1.50	$CDCl_3$	29

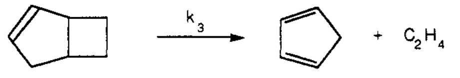
[a] Exo/endo (17:83) H at C6,7 (**1**-d_2, **1**-d_8) or at C7(**1**-d_3); bath temperature 276 °C. [b] To shift H_2O signal from chemical shift region of interest.

Deuterium-labeled versions of **1** were prepared from bicyclo[3.2.0]hepta-2,6-diene (**3**), **3**-*6-d*, and **3**-*1,2,3,4,4,5-d*$_6$[6] through deuteriodiimide reductions (potassium azodicarboxylate; CH_3COOD, 99%-*d*, Norrel); the exo/endo proton intensity at C6,7 (or, in **1**-d_3, at C7) was 17:83 according to ^1H NMR analyses in $CDCl_3$: in **1** the C6,7 endo hydrogens are at 1.63 ppm while the exo hydrogens are centered at 2.13 and 2.28 ppm.[7] Only one other hydrogen in **1** overlaps these absorptions, near 2.15, a complication not present in the **1**-d_8 olefin.



The **1**-d_i compounds were purified by gas chromatography on an SE 30 column and heated at 276 °C in a 1-L Pyrex kinetic bulb with 2-methylpentane as a bath gas to give total pressures of 28–50 Torr. After several hours or several days products **2**-d_i were isolated and purified by gas chromatography on a β,β'-ODPN column; ^1H NMR spectra[8] and integrations were secured with $CDCl_3$ or CD_3OD solutions at 500 MHz. The observed exo/endo C5,6 proton intensity ratios and the derived percent retention values are summarized in Table I. Under the given reaction conditions, the [1,3] CHD-carbon shift occurs with 24 ± 4% retention.

Recovered samples of **1**-d_i showed no loss of stereochemistry at C7. 1,2-Dideuterioethene product from **1**-d_2 and **1**-d_8 was found by infrared spectroscopic analyses to be 33 ± 2% the *Z* isomer.[9] Norbornene-5,6-*cis*-d_2 gives (*Z*)-ethene-d_2 exclusively,[10] and a kinetic study of the thermal isomerizations of **1** with use of dynamic isotope dilution techniques has shown that $k_1 \approx k_3$ (direct reaction of **1** to C_5H_6 and C_2H_4).[10]



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The rearrangement of **1** to **2** occurs not only with predominant inversion but also with an unmistakably substantial retention component; the shift with inversion at the migrating carbon is not energetically advantaged sufficiently to be overwhelmingly preeminent.

Independent experimental demonstration of a substantial retention component for the isomerization **1** to **2** has been attained by Klärner and co-workers.[11]

Acknowledgment. We thank the National Science Foundation for financial support and Professor F.-G. Klärner for sharing results in advance of publication.

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[5] Walsh, R.; Wells, J. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 52–55.

[6] Baldwin, J. E.; Belfield, K. D. *J. Org. Chem.* **1987**, *52*, 4772–4776.

[7] Leigh, W. J.; Srinivasan, R. *J. Org. Chem.* **1983**, *48*, 3970–3979.

[8] For ^1H NMR assignments in **2**, see: Franzus, B.; Baird, W. C., Jr.; Chamberlain, N. F.; Snyder, E. I. *J. Am. Chem. Soc.* **1968**, *90*, 3721–3724. Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 3724–3731. Werstiuk, N. H. *Can J. Chem.* **1970**, *48*, 2310–2313.

[9] Based on absorption intensities at 843 cm^{-1} (*Z* isomer) and 987 cm^{-1} (*E* isomer), with calibration data from S. J. Cianciosi (personal communication) and from Cannarsa, M. J. Ph.D. Thesis, Cornell University, 1984.

[10] Baldwin, J. E.; Belfield K. D., unpublished.

[11] Klärner, F.-G.; Drewes, R.; Hasselmann, D. *J. Am. Chem. Soc.*, following paper in this issue.

Stereochemistry of the Thermal Rearrangement of Bicyclo[3.2.0]hept-2-ene to Bicyclo[2.2.1]hept-2-ene (Norbornene): [1,3] Carbon Migration with Predominant Inversion

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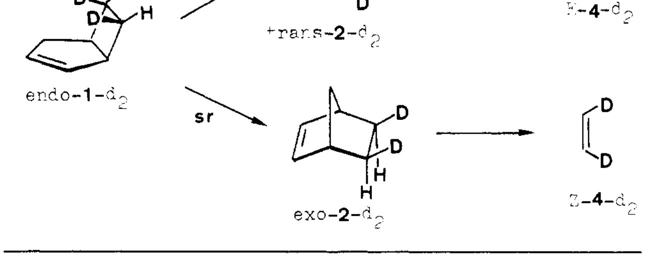
The thermal isomerization of bicyclo[3.2.0]hept-2-ene (**1**) to norbornene (**2**) has attained considerable interest in connection with the theory of sigmatropic rearrangements.[1] The stereochemical course only known for the isomerization of derivatives of **1** is strongly dependent on the substituents at the migrating carbon atom C-7.[2] Consistent with the Woodward–Hoffmann rules[1] *exo*-7-deuterio- and *exo*-7-methyl-*endo*-bicyclo[3.2.0]hept-2-en-6-yl acetate rearrange predominantly with inversion at C-7 (si: 95 and 91%, respectively), whereas a migration with preferential retention at C-7 (sr: 88%) occurs in the *endo*-7-methyl derivative.[2a] Accordingly the isomerization of **1** seems to be a borderline case where concerted and nonconcerted pathways may be competitive.



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[1] Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511–2513. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim/Bergstr., 1970.

[2] (a) Berson, J. A.; Nelson, G. L. *J. Am. Chem. Soc.* **1967**, *89*, 5503–5504. Berson, J. A. *Acc. Chem. Res.* **1968**, *1*, 152–160; **1972**, *5*, 406–414. Berson, J. A.; Holder, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 2037–2038. Wilson, S. R.; Mao, D. T. *J. Chem. Soc., Chem. Commun.* **1978**, 479–480. Review: Berson, J. A. in *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 311–390. (b) Hasselmann, D. *Angew. Chem.* **1975**, *87*, 252–253; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 257–258.

0002-7863/88/1510-0297$01.50/0