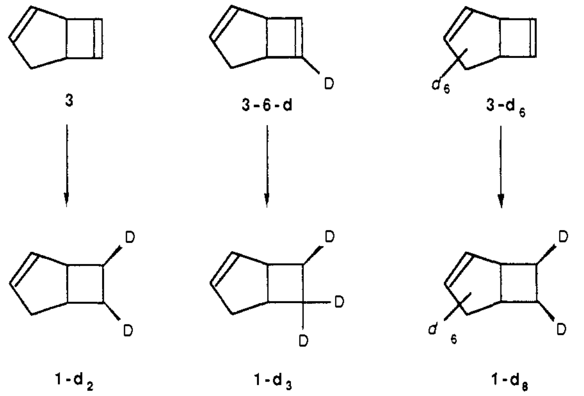
Table I. Stereochemistry of [1,3] Carbon Shifts in Isomerizations of Deuteriated Bicyclo[3.2.0]hept-2-enes to Bicyclo[2.2.1]hept-2-enes

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

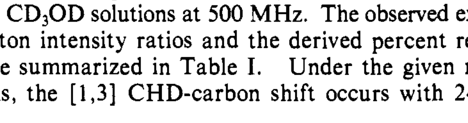
[a] Exo/endo (17:83) H at C6,7 (**1**-d_2, **1**-d_8) or at C7(**1**-d_3); bath temperature 276 °C. [b] To shift H_2O signal from chemical shift region of interest.

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]



1

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.

---

(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.

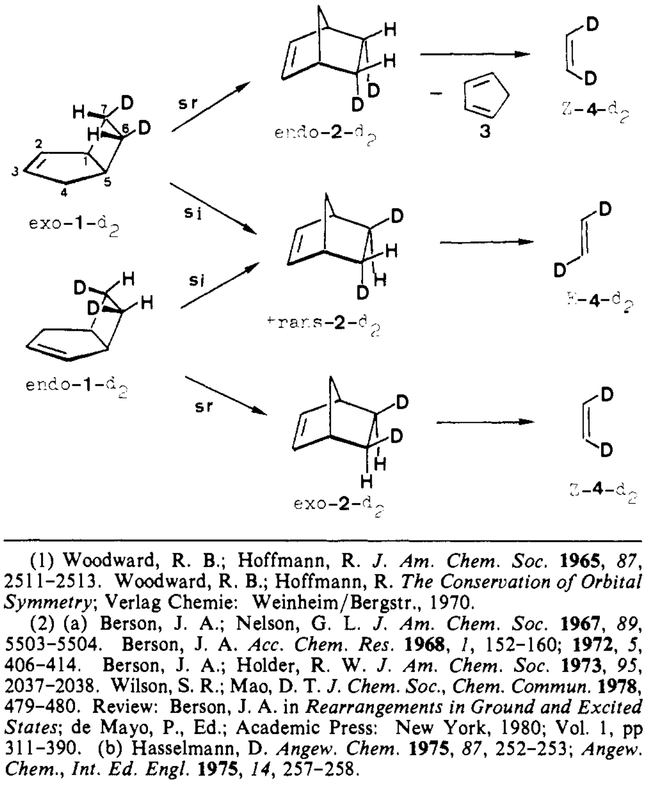
Stereochemistry of the Thermal Rearrangement of Bicyclo[3.2.0]hept-2-ene to Bicyclo[2.2.1]hept-2-ene (Norbornene): [1,3] Carbon Migration with Predominant Inversion

Frank-Gerrit Klärner,* Rolf Drewes, and Dieter Hasselmann

Fakultät für Chemie der Ruhr-Universität
Postfach 10 21 48, D-4630 Bochum 1
Federal Republic of Germany

Received September 22, 1987

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.



---

(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

Table I. ^{1}H NMR (400 MHz, C_6D_6) and ^{2}H NMR (61.4 MHz, CCl_4)

		rel signal intensity			
	δ ppm[a]	starting **1**-d_l		recovered **1**-d_l[b]	
H or D	(C_6D_6)	^{1}H NMR	^{2}H NMR	^{1}H NMR	^{2}H NMR
endo-6,7	1.65	1.947	0.123	1.890	0.163
endo-4 exo-6	2.05 2.10	1.345	1.038	1.314	1.019
exo-7	2.20	0.348	1.000	0.419	1.000
exo-4	2.45	0.998	0.076	0.967	0.074
5	2.72	1.000	0.009	1.000	0.012
1	3.15	0.984	0.019	0.979	0.016
2,3	5.70 5.75	1.897	0.047	1.914	0.047

[a] The signals for **1** were assigned by COSY 2D NMR and double resonance experiments. [b] From the thermolysis at 312 °C.

Table II. ^{1}H NMR (400 MHz, C_6D_6) and ^{2}H NMR (61.4 MHz, CCl_4) of **2**-d_l

	δ ppm[a]	rel signal intensity	
H or D	(C_6D_6)	^{1}H NMR	^{2}H NMR
endo-5,6	0.94	1.222	1.000
anti-7	1.03	1.105	0.011
syn-7	1.29	1.000	0.016
exo-5,6	1.55	1.365	0.828
1,4	2.80	1.963	0.044
2,3	5.90	1.929	0.039

[a] For the ^{1}H NMR assignments in **2** see ref 9.

We have studied the stereochemical course of the [1,3] shift in the parent bicyclo[3.2.0]hept-2-ene only labeled by deuterium. Its experimental realization turned out to be difficult since at about 300 °C—the temperature required for the isomerization of **1**—norbornene (**2**) undergoes a retro-Diels–Alder reaction to give 1,3-cyclopentadiene (**3**) and ethene (**4**). Thus the maximum concentration of **2** to be expected is only about 1%.[3]

Catalytic reduction of bicyclo[3.2.0]hepta-2,6-diene (**5**)[4] with 1 mol equiv of deuterium (10% Pt/C, ether, room temperature) led to a mixture of deuteriated bicyclo[3.2.0]heptene **1**-d_l, bicyclo[3.2.0]heptane, and unconverted **5** in a (63:15:22) ratio as analyzed by GC.[5] From the ^{1}H and ^{2}H NMR spectrum of **1**-d_l isolated by preparative GC (Table I) the exo/endo selectivity in the deuteriation of the cyclobutene double bond is determined to be 96:4 and 94:6, respectively.[6a]

Thermolysis of **1**-d_l at 312 °C (240 min, gas phase, with cyclohexane as internal standard) produced a mixture of isomers: **1**-d_l (34%), norbornene **2**-d_l (1.3%), and five unidentified compounds (11%);[7] the only other products were cyclopentadiene (**3**) and deuteriated ethene (**4**-d_l). The deuterium distribution in **1**-d_l and **2**-d_l separated by GC[5] was again determined by ^{1}H and ^{2}H NMR spectroscopy (Tables I and II). The only slightly changed exo/endo ratio of deuterium at C-6,7 in recovered **1**-d_l (^{1}H NMR, 91:9, ^{2}H NMR, 93:7) shows that epimerization at C-6 and/or C-7 does not compete with the 1,3 shift to a significant extent. The stereochemical course of the 1,3 shift can now be calculated from the endo/exo ratio of deuterium at C-5,6 in the norbornene product **2**-d_l (Table II: ^{1}H NMR, 1.22; ^{2}H NMR, 1.21). Accordingly, the isomerization of **1** to **2** occurs with 89% inversion. An independent evidence for the predominant inversion process results from the *E*:*Z* ratio of the 1,2-dideuterioethene product which was analyzed by its characteristic IR bands at 987 and 843 cm^{-1} [8] to contain (82 ± 4)% of the *E* isomer.[6b]

The [1,3] rearrangement in the parent system shows a stereochemical course comparable with the classical example of *exo*-7-deuterio-*endo*-bicyclo[3.2.0]hept-2-en-6-yl acetate already mentioned.[2a] Obviously the acetoxy group at C-6 has only a minor effect on the stereochemistry of the [1,3] shift. The substantial component of retention (11%) observed here indicates that orbital symmetry cannot be the only factor which controls the course of reaction. As a reasonable explanation we suggest that a nonconcerted diradical pathway competes with the concerted process.[10,11] Similar results for the isomerization of **1** to **2** have been obtained independently by Baldwin and Belfield.[12]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and Professor J. E. Baldwin for sharing results in advance of publication.

---

[3] Cocks, A. T.; Frey, H. M. *J. Chem. Soc. A* **1971**, 2564-2566. Walsh, R.; Wells, J. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 52-55.

[4] Dauben, W. G.; Cargill, R. L. *Tetrahedron* **1961**, *12*, 186-189. Bicyclo[3.2.0]hepta-2,6-diene was prepared by reductive elimination of 6,7-dichlorobicyclo[3.2.0]hept-2-ene by using potassium in ether. Bartlett, P. D.; Helgeson, R.; Wersel, O. A. *Pure Appl. Chem.* **1968**, 187-200.

[5] GC analyses were performed on a 40-m silicon oil OV 101 glass capillary column at 25 °C. The products of catalytic reduction and thermolysis were separated on a 4-m squalane column at 78 °C.

[6] (a) The exo/endo selectivity in the catalytic deuteriation of norbornadiene proved to be 94:6. Thermolysis of the deuteriated norbornene product at 312 °C gave (*Z*)-1,2-dideuterioethene (≥97%). (b) The *E*:*Z* ratio in **4**-d_2—the product from the thermolysis of **1**-d_l—does not deviate from the inversion/retention ratio found in **2**-d_2 significantly within the limits of error of the IR analysis. Thus only a minor component of **4**-d_2 might stem directly from **1**-d_2.

[7] The unidentified compounds could be secondary products from the cleavage of cyclobutane bonds C-1–C-5 and C-6–C-7 in **1**, see ref 3.

[8] Calibration data reported in the dissertation by Cannarsa (Cannarsa, M. J. *The Synthesis and Thermolysis of Stereospecifically Labeled 1,2,3,4-Cyclobutanes-d_4*; Cornell University, 1984) were used for the IR analysis of the *E*:*Z* ratio of 1,2-dideuterioethene.

[9] 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.

[10] As an alternative interpretation a stereoselective diradical process cannot be excluded as has also been suggested for the [1,3] shift in substituted bicyclo[2.1.1]hex-2-ene systems. Newman-Evans, R. H.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 7994-7995. Carpenter, B. K. *J. Am. Chem. Soc.* **1985**, *107*, 5730-5732.

[11] According to a thermochemical estimate the enthalpy of formation of the transition state ($\Delta H_f°(\text{TS}) = \Delta H_f°(\mathbf{1}) + \Delta H^*(\mathbf{1} \rightarrow \mathbf{3} + \mathbf{4}) = 28.6 + 49.2^3 = 77.8$ kcal/mol) is higher by 1.3 kcal/mol than that of the corresponding diradical calculated by molecular mechanics; thus the energy of concert for reaction **1** → **2** appears to be negligible: Doering, W. v. E.; Roth, W. R.; Breuckmann, R.; Figge, L.; Lennartz, H.-W.; Fessner, W.-D.; Prinzbach, H. *Chem. Ber.*, in press. $\Delta H_f°(\mathbf{1})$ was determined from the heat of hydrogenation of **1** ($\Delta H_H = -27.9$ kcal/mol) and a MM2 calculation of $\Delta H_f°$ (bicyclo[3.2.0]heptane). Roth, W. R.; Lennartz, H.-W., unpublished results.

[12] Baldwin, J. E.; Belfield, K. D. *J. Am. Chem. Soc.*, preceding paper in this issue.

Synthesis by Spontaneous Self-Assembly of Metal Atom Clusters of Zirconium, Niobium, and Tantalum

F. Albert Cotton,* Piotr A. Kibala, and Wieslaw J. Roth

Department of Chemistry and
Laboratory for Molecular Structure and Bonding
Texas A&M University
College Station, Texas 77843

Received October 1, 1987

Systematic, designed preparative methods for obtaining metal atom cluster species are obviously desirable but rarely devised. However, spontaneous self-assembly occurs and can be exploited. We report here three such reactions, each of which leads to a product that is of unusual interest in its own right and also possesses potential for further synthetic development.

There are several previous reports of trinuclear, triangular cluster species of niobium comprising both the bicapped[1] $[Nb_3(\mu_3\text{-}O)_2]$ and $Nb_3(\mu_3\text{-}X)(\mu\text{-}X)_3$ type cores. Most recently we described the compound $Nb_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3Cl_3(PMe_2Ph)_6$[2] which has an eight-electron core configuration and a mean Nb–Nb

---

[1] Cotton, F. A.; Diebold, M. P.; Llusar, R.; Roth, W. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1276.

[2] Cotton, F. A.; Diebold, M. P.; Roth, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 2833.

0002-7863/88/1510-0298$01.50/0