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Secondary Deuterium Kinetic Isotope Effects at the Termini of *cis*-1,2-Divinylcyclopropane and *cis*-1,2-Divinylcyclobutane in Their 3,3-Sigmatropic Shifts: Evidence for Different Transition-State Structures

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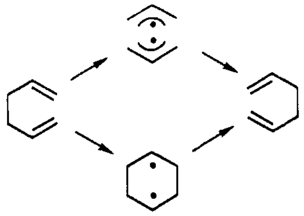
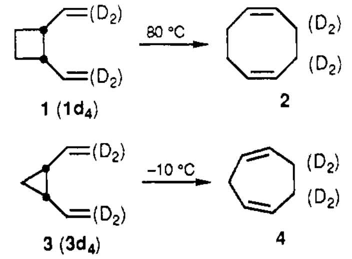
In an effort to understand the substantially lower activation energy for the 3,3-sigmatropic shift of *cis*-1,2-divinylcyclopropane relative to that of *cis*-1,2-divinylcyclobutane, we determined the secondary deuterium kinetic isotope effects (KIEs) at the vinyl termini of both materials. For the cyclopropane derivative, $k^{H}/k^{d4} = 1/1.29$ (±0.09) at 10 °C in deuteriochloroform. For the cyclobutane derivative, $k^{H}/k^{d4} = 1/1.04$ (±0.02) at 77.7 °C in hexachlorobutadiene solvent. These KIEs indicate that there is much more bonding at the terminal carbons in the transition state for the rearrangement of the cyclopropane analogue and relatively little bonding at the termini in the rearrangement of the cyclobutane material.

Introduction

The spectacularly fast 3,3-sigmatropic shift of *cis*-1,2-divinylcyclopropane systems[1] presents a challenge to understand substituent rate effects. In general, the transition-state structure for 3,3-shifts varies with substitution as judged by secondary deuterium kinetic isotope effects (KIEs).[2] Some success in correlating substituent rate effects has been achieved by using the free energies of formation of the 3,4-bond-breaking and the 1,6-bond-making transition-state alternatives (two allyls and cyclohexane-1,4-diyl, respectively) along with the free energy of reaction as parameters to determine the energy surface based on a hyperbolic paraboloid model.[2c,d]

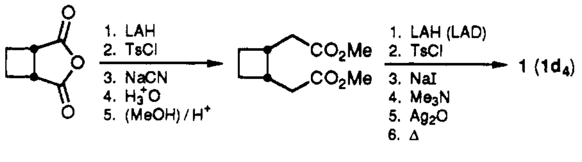


After the usual mathematical manipulations to find the saddle point, a single constant suffices to determine its height relative to reactant. The position of the saddle point generally correlates with the magnitudes of normal KIEs at the 3,4-positions and with the magnitudes of the inverse KIEs at the 1,6-positions. The correlation equations, however, are inadequate with *cis*-1,2-divinylcyclopropane derivatives.[2d] In particular, these reactions are much faster than expected, assuming that the bond-breaking and bond-making activation free energies are the same as those with *cis*-1,2-divinylcyclobutane 3,3-shifts whose rates do correlate when the same constant appropriate to other 3,3-shifts is used. Thus the activation energy for the conversion of *cis*-1,2-divinylcyclopropane (**3**) to *cis,cis*-1,4-cycloheptadiene (**4**)[3a] is 4.5 kcal/mol lower than that for reaction of *cis*-1,2-divinylcyclobutane (**1**)[4a] to *cis,cis*-1,5-cyclooctadiene (**2**), and both have similar preexponential factors. It is reasonable that the bond breaking alternative is the same in both the three- and four-membered-ring cases since the strain energy in the two starting materials is nearly the same. Reinforcing this conclusion is the fact that the rates of geometric isomerization of the trans isomers of **1**[3d] and **3**[4a] are nearly identical; indeed, the activation free energy of this process is the free energy change for the bond-breaking alternative. It is not clear that the energy of the bond-making transition-state alternative (cyclohexane-1,4-diyl) is the same in the three- and four-membered-ring cases, so the KIEs at the terminal positions of **1** and **3** were examined to provide information on the point.



Results

cis-1,2-Divinylcyclobutane (**1**) and *cis*-1,2-bis(2′,2′-dideuterio-1′-vinyl)cyclobutane (**1d4**) were prepared from 1,2-cyclobutanedicarboxylic anhydride. The ditosylate formed by lithium aluminum hydride reduction and reaction with tosyl chloride was converted to the dinitrile with sodium cyanide in DMSO. The ditosylate resulting from nitrile hydrolysis, esterification, reduction (with LAH or LAD), and reaction with tosyl chloride was treated with sodium iodide in acetone, then with trimethylamine, and then with silver oxide. Thermal elimination of the hydroxide gave material identical in all respects with that synthesized by Vogel.[4b] The deuterated material had less than 2% of protium at the terminal positions.



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[1] Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press; New York, NY, 1981.

[2] (a) Humski, K.; Malojčić, R.; Borčić, S.; Sunko, D. E. *J. Am. Chem. Soc.* **1970**, *92*, 6534. (b) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693. (c) Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142. (d) Gajewski, J. J.; Gilbert, K. E. *J. Org. Chem.* **1984**, *49*, 11.

[3] (a) Schneider, M. *Angew. Chem.* **1975**, *87*, 717. Schneider, M. P.; Rebell, J. *J. Chem. Soc., Chem. Commun.* **1975**, 283. (b) For isolation and kinetics of reaction of *cis*-1,2-divinylcyclopropane, see: Brown, J. M.; Golding, B. T.; Stofko,jun, J. J. *Ibid.* **1978**, 319; *J. Chem. Soc., Perkin Trans. 2* **1978**, 436. (c) For the first description of this 3,3-shift, see: Doering, W. von E.; Roth, W. R. *Tetrahedron* **1963**, *19*, 715. (d) For the kinetics of reaction of the trans isomer, see: Mannosuke, A.; Crawford, R. J. *Can. J. Chem.* **1972**, *50*, 2158.

[4] (a) Hammond, G. S.; DeBoer, C. D. *J. Am. Chem. Soc.* **1964**, *86*, 899. (b) For the first description of this 3,3-shift, see: Vogel, E. *Justus Liebigs Ann. Chem.* **1958**, *615*, 1.

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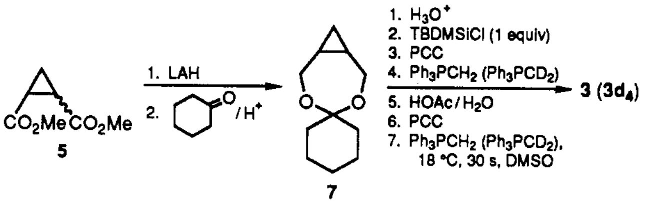
Duplicate pyrolyses of **1** and **1d4** in hexachlorobutadiene solvent in separate NMR tubes immersed simultaneously in a bath held at 77.7 °C were followed by ^{1}H NMR to give $k^1/k^{1d4} = 1/1.04$ (±0.02). The individual rate constants had less than 3% standard deviation in the least-squares determination and had correlation coefficients greater than 0.999.

cis-1,2-Divinylcyclopropane (**3**) and *cis*-1,2-bis(2′,2′-dideuterio-1′-vinyl)cyclopropane (**3d4**) were prepared in 10 steps from methyl chloroacetate and methyl acrylate. An 82:12 mixture of *cis*/*trans*-1,2-dicarbomethoxycyclopropane was prepared by a modification of a procedure by McCoy.[5] Separation of the isomers was accomplished after reduction by selective reaction with cyclohexanone in acid. The cis diol ketal was hydrolyzed, monoprotected with TBDMSiCl, oxidized with PCC, reacted with methylene- or (dideuteriomethylene)triphenylphosphorane, deprotected, oxidized with PCC, and reacted again with methylene- or (dideuteriomethylene)triphenylphosphorane. The latter reaction was accomplished in DMSO solvent at 18 °C for 30 s, after which the diolefin was removed under vaccum and collected at 77 K in a receiver containing deuteriochloroform.



The rates of rearrangement of **3** and **3d4** were determined in an NMR probe held reproducibly at 10.0 (±0.1) °C. The decrease in the syn H on C-2 and the increase of the signal corresponding to the two hydrogens on C-3 of the product 1,4-cycloheptadiene (**4**) were followed.[6] Four or five runs were conducted with each starting material, each giving a rate constant with an average deviation of 3–4%. The deviations in the rate constants for the individual runs were less then the deviation in the average rate constant. After correction for the deuterium incorporation, $k^{3H}/k^{3d4} = 1/1.29$ (±0.09).

Discussion

The rates of pyrolytic reaction of *trans*-1,2-divinylcyclopropane and *trans*-1,2-divinylcyclobutane are similar, and the reactions are generally assumed to proceed via homolytic fission to biradicals as opposed to giving Cope rearrangement product directly. This is probably the case since the termini of the diene system cannot easily approach one another although some direct reaction may occur with *trans*-divinylcyclobutane.[7] The negative activation entropies and faster rates of reaction of **1** and **3** suggest concert, but the faster rate of **3** (by roughly 4.5 kcal/mol) suggests an added factor. Further, the very fast rates of the degenerate 3,3-shift in homotropilidene,[8] bullvalene,[9] and semibullvalene[10] have no parallel in cyclobutane 3,3-shifts except in highly strained systems.

The KIEs determined at the terminal carbons for the 3,3-shifts of **1** and **3** indicate very different transition states for the two reactions. In particular, the KIEs suggest that there is much more bonding at the terminal carbons in the transition state for the rearrangement of **3**. To quantify this difference it is important to compare the KIEs to the equilibrium isotope effect (EIE) at the temperature of the reaction. This is done by reference to the equation determined by Conrad, who correlated Cope rearrangement EIEs over a wide temperature range:[11]

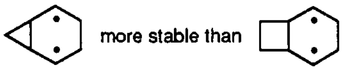
$$CH_2{=}CHCH_2CH_2CH{=}CD_2 \rightleftharpoons CH_2{=}CHCH_2CD_2CH{=}CH_2$$

$$\log K^{H}/K^{d2} = 291.6/2.3RT - 0.0818$$

Of course, the EIE calculated must be squared in order to make the comparison. To the extent that there exists a linear free energy relationship (LFER) between the KIEs and EIEs, i.e., KIE = EIE^i, the exponent is 0.05 (±0.05) for the bond making with **1** at 77.7 °C, and 0.39 (±0.09) is the exponent for the bond-making KIE with **3** at 10.0 °C.

From the small bond-making KIE, the transition state for the 3,3-shift of **1** looks much more like the bisallyl diradical than the 1,4-diyl although it cannot be the bisallyl species if that is the species generated at higher temperatures in the pyrolysis of the trans isomer of **1**. More likely, the transition state for it is a delocalized one that resembles reactant, recognizing that this rearrangement is probably 10–15 kcal/mol exothermic.

The relatively larger bond-making KIE with **3** is probably related to the faster rates of 3,3-shift of **1** and possibly to those of other *cis*-1,2-divinylcyclopropanes. It is tempting to simply argue that the cyclopropane ring bond is more effective in conjugating with the 1,4-diyl to stabilize this alternative in a delocalized transition state.



The large body of work by Berson and others summarized by Engel[12] on cyclic azo compounds reveals the fact that a cyclopropane ring acts like a double bond to stabilize a delocalized transition state for thermal loss of nitrogen whereas a cyclobutane ring has no comparable effect. It must be emphasized that the magnitude of the bond-making KIE with **3** is not consistent with complete bond making in the form of a cyclohexane-1,4-diyl transition state or shallow minimum, as has been suggested by Dewar

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[5] McCoy, L. L. *J. Am. Chem. Soc.* **1958**, *80*, 6568.

[6] This region from δ 0.55 to 0.80 was integrated to follow the loss of **3**, see ref 3b; the region from δ 2.7 to 3.0 was integrated to follow the increase in cycloheptadiene. The mole fraction of **3** remaining was calculated from the ratio (δ 0.55–0.80)/[(δ 0.55–0.80) + 0.5 (δ 2.7–3.0)]. The times for spectral acquisition were determined by manually timing the events since the spectrometer did not record the time to store each spectrum and to rezero the computer. The first two spectra of each run were discarded in order to allow for warm-up. Further, all spectra in which the mole fraction of **3** was below 0.20 were discarded because of error in integrating small peaks.

[7] Martin, H.-D.; Eisenmann, E.; Kunze, H.; Bonacič-Koutecký, V. *Chem. Ber.* **1980**, *113*, 1153.

[8] See ref 3c and see: Günther, H.; Pawliczek, J. B.; Ulman, J.; Grimme, W. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 517; *Chem. Ber.* **1975**, *108*, 3141. See also: Bicker, R.; Kessler, H.; Ott, W. *Ibid.* **1975**, *108*, 3151.

[9] (a) Günther, H.; Ulmen, J. *Tetrahedron* **1974**, *30*, 3781 and reference contained therein. (b) For the first synthesis of bullvalene, see: Schröder, G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 481.

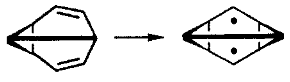
[10] (a) Cheng, A. K.; Anet, F. A. L.; Mioduski, J.; Meiwald, J. *J. Am. Chem. Soc.* **1974**, *96*, 2887. (b) For the first synthesis of semibullvalene, see: Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183.

[11] Conrad, N. D. Ph.D. Thesis, Indiana University, 1978. Gajewski, J. J. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: New York, 1987; Vol. 7, p 61. There are unfortunate typos in Appendix B: the ratio of the hydrogen–deuterium equilibrium constants must be reversed, and the equations refer to two deuteriums, not four.

[12] Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

for the Cope rearrangement of the parent system.[13] Recently, Dewar has examined the 3,3-shifts of bullvalene, barbaralane, and semibullvalene and concluded that the transition states for these is "aromatic", that is, they have delocalized transition states with roughly 2.2-Å bonds between the originally bonded atoms and between the atoms that will form a cyclopropane bond.[14] Thus these transition states have a substantial component of bond breaking, probably more than with the parent compound, **3**, because bond making in these polycyclic cases necessarily generates a cyclopropane ring whose ring strain is roughly 27 kcal/mol.

e.g.,



A final point for consideration is the relative exothermicity of the 3,3-shifts of **1** and **3**. Molecular mechanics calculations suggest that the reaction of **3** is 6 kcal/mol more exothermic than that of **1** (−20 vs −14 kcal/mol).[2d] In large part this is due to the increased strain energy of cyclooctadiene relative to cycloheptadiene. It is not clear to exactly what extent the reaction exothermicity affects the reaction rate in pericyclic reactions although there is the suggestion from the previous work that only one-quarter of the exothermicity is reflected in the transition-state energy. Thus the rate difference between **1** and **3** is in only a small part due to the relative exothermicities. It is also true that the transition state for reaction of **3** should be more reactant-like than that from **1**. The finding of more bond making with **3** therefore is even more surprisingly for an early transition state.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Nicolet NT 360 or a Varian XL 300 spectrometer. ^{13}C NMR spectra were recorded on a Varian XL 300 spectrometer at 75.43 MHz. Chemical shifts are reported in parts per million downfield from tetramethylsilane. All spectra were taken in deuteriochloroform unless otherwise noted. Infrared spectra were taken on a Perkin-Elmer Model 298 spectrometer. Analytical gas chromatography was performed by using a Varian 3700 GC instrument fitted with a 50 m × 0.25 mm ID DB-5 fused silica capillary column, a flame-ionization detector and a Hewlett-Packard Model 3390-A integrator. Preparative gas chromatography was performed on a Varian aerograph.

1,2-Dicarbomethoxycyclopropane (5). In a modification of the McCoy[5] procedure, a solution of methyl acrylate (86.0 g, 1.00 mol) and methyl chloroacetate (108.5 g, 1.00 mol) was added with stirring to a suspension of toluene (250 mL) and a 50% dispersion of sodium hydride in mineral oil from a previously opened can containing white flecks (60.0 g, 1.25 mol). After being stirred for 18 h at room temperature, the mixture was cooled in an ice bath. Methanol (38 g, 1.2 mol) was added at such a rate as to maintain the temperature between 10 and 18 °C. Water (500 mL) and diethyl ether (300 mL) were added. The organic phase was washed with water and dried (MgSO$_4$). Fractional distillation (85–87 °C, 1 Torr) gave 57.1 g (0.36 mol, 36% yield) of a mixture of cis and trans diesters. Capillary GC indicates that the mixture is 17.8% trans and 82.2% cis. ^{1}H NMR (361 MHz): δ 1.26 (td, *J* = 8.4, 5.0 Hz, 0.8 H), 1.45 (t, *J* = 7.2 Hz, 0.4 H), 1.68 (td, *J* = 6.6, 5.1 Hz, 0.8 H), 2.08 (dd, *J* = 8.4, 6.7 Hz, 1.6 H), 2.18 (t, *J* = 7.2 Hz, 0.4 H), 3.70 (s, 6 H). IR (neat): 3004, 2953, 1733, 1438, 1195, 1171 cm^{-1}. Decoupled ^{13}C NMR: δ (intensity) 11.60 (82), 15.14 (25), 21.19 (199), 22.00 (56), 51.93 (166), 170.17 (40), 171.98 (14). Gated decoupled ^{13}C NMR: δ 11.60 (t, *J* = 166 Hz), 15.14 (t, *J* = 169 Hz), 21.19 (d, *J* = 167 Hz), 22.00 (d, *J* = 173 Hz), 51.93 (q, *J* = 147 Hz), 170.17 (s), 171.98, (s).

1,2-Bis(hydroxymethyl)cyclopropane (6). To a suspension of lithium aluminum hydride (8.23 g, 220 mmol) and diethyl ether (400 mL) was added with stirring, a solution of *trans*-1,2-dicarbomethoxycyclopropane (5.1 g, 32 mmol) and *cis*-1,2-dicarbomethoxycyclopropane (23.5 g, 150 mmol) in diethyl ether (100 mL). The mixture was stirred for 14 h and then quenched by dropwise addition of 8.2 g of water, then of 8.2 g of 15% sodium hydroxide, and finally of 24.6 g of water. Sulfuric acid (10%, 550 g) was then added to dissolve the solids. Material from an equivalent reaction was added to this reaction mixture, and sodium chloride (300 g) was added. This solution was continuously extracted with diethyl ether for 36 h. The diethyl ether was removed by rotary evaporator. The diols were dissolved in methylene chloride and dried (MgSO$_4$). Distillation (103 °C, 1 Torr) gave 22.9 g (0.24 mol, 70% yield) of a mixture of cis and trans diols. Capillary GC indicates that the mixture is 82.6% cis and 17.4% trans. ^{1}H NMR (361 MHz) (CD$_3$COCD$_3$): δ 0.22 (q, *J* = 5.3 Hz, 0.8 H), 0.38 (t, *J* = 6.7 Hz, 0.4 H), 0.71 (td, *J* = 8.2, 5.1 Hz, 0.8 H), 0.89–0.97 (m, 0.4 H), 1.17–1.26 (m, 1.6 H), 3.23–3.46 (m, 0.8 H), 3.33–3.46 (m, 0.8 H), 3.89 (dd, *J* = 11.7, 5.4 Hz, 1.6 H).[15] IR (neat): 3340, 3010, 2890, 1425, 1250, 1148, 1019 cm^{-1}.

Cyclohexanone Ketal of *cis*-1,2-Bis(hydroxymethyl)cyclopropane (7). A solution of cis diol (18.7 g, 184 mmol), trans diol (4.0 g, 39 mmol), cyclohexanone (60 g, 610 mmol), *p*-toluenesulfonic acid monohydrate (0.05 g, 0.3 mmol), and benzene (400 mL) was refluxed for 6 h with water removal via Dean–Stark apparatus. This solution was washed thrice with 15% sodium hydroxide. After drying (MgSO$_4$), distillation (95 °C, 0.5 Torr) gave 27.3 g (0.15 mol, 82% yield based on cis diol) of **7**. ^{1}H NMR (361 MHz): δ 0.65 (apparent t, *J* = 7.1 Hz, 2 H), 1.06–1.15 (m, 2 H), 1.33–1.75 (m, 10 H), 3.73, 4.13 (A, A′, B, B′) (major *J* = 13.6, 13.0 Hz, 4 H). Gated decoupled ^{13}C NMR: δ 8.8 (t, *J* = 160 Hz), 16.8 (d, *J* = 159 Hz), 22.7 (t, *J* = 125 Hz), 22.8 (t, *J* = 127 Hz), 32.7 (t, *J* = 127 Hz), 33.6 (t, *J* = 127 Hz), 60.9 (t, *J* = 143 Hz), 102.2 (s). IR (neat): 3070, 3000, 2940, 1460, 1448, 1366, 1161, 1117, 1091, 996 cm^{-1}.

***cis*-1,2-Bis(hydroxymethyl)cyclopropane (8).** Ketal **7** (27.2 g, 150 mmol), acetic acid (71.9 g, 1.2 mol), and water (35.9 g, 2.0 mol) were stirred at room temperature for 24 h. The solution was cooled to 0 °C, and sodium hydroxide (50 g, 1.3 mol) was added. The solution was saturated with sodium chloride and continuously extracted with diethyl ether for 24 h. The diethyl ether was removed via rotary evaporator, and the cis diol was dissolved in methylene chloride. After drying (MgSO$_4$), fractional distillation (105 °C, 0.5 Torr) gave 13.0 (0.127 mol, 85% yield) of cis diol. ^{1}H NMR (361 MHz): δ 0.22 (q, *J* = 5.3 Hz, 1 H), 0.82 (td, *J* = 8.2, 5.1 Hz, 1 H), 1.26–1.40 (m, 2 H), 3.08 (br s, 2 H), 3.18–3.31 (m, 2 H), 4.11 (dd, *J* = 11.7, 5.4 Hz, 2 H). Gated decoupled ^{13}C NMR (CD$_3$COCD$_3$): δ 8.58 (t, *J* = 161 Hz), 18.50 (d, *J* = 160 Hz), 62.83 (t, *J* = 140 Hz).

***cis*-2-(Hydroxymethyl)-1-[(*tert*-butyldimethylsiloxy)methyl]cyclopropane (9).** To a 0 °C solution of *tert*-butyldimethylsilyl chloride (19.2 g, 127 mmol) and methylene chloride (350 mL) were added triethylamine (26 g, 0.26 mol) and **8** (12.95 g, 0.127 mol). After 2 h at 0 °C, a white precipitate had formed. After washing (water) and drying (MgSO$_4$), **9** (24.2 g, 0.113 mol, 89% yield) was obtained by fractional distillation (105 °C, 1 Torr). ^{1}H NMR (361 MHz): δ 0.10 (s, 3 H), 0.12 (s, 3 H), 0.20 (apparent q, *J* = 5.3 Hz, 1 H), 0.76 (td, *J* = 8.1, 5.1 Hz, 1 H), 0.92 (s, 9 H), 1.18–1.30 (m, 1 H), 1.30–1.43 (m, 1 H), 3.19–3.31 (m, 3 H), 3.97 (dd, *J* = 12.1, 5.3 Hz, 1 H), 4.15 (dd, *J* = 11.6, 5.4 Hz, 1 H). Gated decoupled ^{13}C NMR: δ −5.62 (q, *J* = 118 Hz), −5.40 (q, *J* = 119 Hz), 8.34 (t, *J* = 161 Hz), 17.29 (d, *J* = 161 Hz), 18.07 (d, *J* = 161 Hz), 25.74 (q, *J* = 124 Hz), 63.01 (t, *J* = 144 Hz), 63.80 (t, *J* = 142 Hz). IR (neat): 3460, 3078, 3010, 2962, 2938, 2883, 2862, 1463, 1254, 1053, 833, 778 cm^{-1}.

***cis*-2-[(*tert*-Butyldimethylsiloxy)methyl]cyclopropanecarboxaldehyde (10).** To a well-stirred mixture of pyridinium chlorochromate (29.2 g, 0.14 mol), sodium acetate (11.1 g, 0.14 mol), Celite (8.8 g), and dry methylene chloride (310 mL) was added **9** (5.90 g, 27.1 mmol) in 50 mL of dry methylene chloride. After 3 h, diethyl ether was added and the mixture was filtered through Florisil. The solution was washed with saturated copper(II) sulfate until the characteristic violet color of the Cu^{2+} pyridine complex no longer appeared. After drying (MgSO$_4$) and

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(13) Dewar, M. J. S.; Jie, C. *J. Am. Chem. Soc.* In press.

(14) Dewar, M. J. S.; Jie, C. *Tetrahedron* **1988**, *44*, 1351.

(15) Baldwin, J. E.; Ullenius, C. *J. Am. Chem. Soc.* **1974**, *96*, 1542.

removal of solvents by rotary evaporation, distillation (101 °C, 1 Torr) gave **10** (5.60 g, 26.2 mmol, 96% yield). ^{1}H NMR (300 MHz): δ 0.041 (s, 3 H), 0.047 (s, 3 H), 0.877 (s, 9 H), 1.22 (td, J = 7.8, 4.9 Hz, 1 H), 1.30–1.38 (m, 1 H), 1.70–1.83 (m, 1 H), 1.91–2.02 (m, 1 H), 3.63 (dd, J = 11.2, 7.6 Hz, 1 H), 3.98 (dd, J = 11.2, 5.4 Hz, 1 H), 9.42 (d, J = 5.0 Hz, 1 H).

The pyridinium chlorochromate used in this oxidation was prepared as described in the literature, with the additional purification step of dissolving the brown-orange solid in 3 times its weight of tetrahydrofuran, and then reprecipitated by addition of 12 times its weight of ethyl acetate. After suction filtration and removal of residual solvents via high vacuum, a yellow-orange solid remained.

***cis*-2-Vinyl-1-[(*tert*-butyldimethylsiloxy)methyl]cyclopropane (11).** To a suspension of methyltriphenylphosphonium bromide (3.90 g, 10.9 mmol) and tetrahydrofuran (60 mL) was added, with stirring, *n*-BuLi in hexane (10.0 mL of a 1.1 M solution). After $^1/_2$ h of stirring, the aldehyde (1.95 g, 9.11 mmol) in THF (20 mL) was added in one portion. Water (140 mL) was added after 1 h. The mixture was extracted with pentane. After drying (MgSO$_4$) and removal of pentane via rotary evaporator, Kugelrohr distillation (140 °C maximum, 1 Torr) gave the very foul smelling alkene (1.80 g, 8.5 mmol, 93% yield). ^{1}H NMR (300 MHz): δ 0.06 (s, 6 H), 0.44 (apparent q, J = 5.4 Hz, 1 H), 0.91 (s, 9 H), 0.87–0.95 (m, 1 H), 1.21–1.36 (m, 1 H), 1.55–1.67 (m, 1 H), 3.62 (qd, J = 16.1, 6.6 Hz, 2 H), 4.95 (dd, J = 10.4, 2.0 Hz, 1 H), 5.12 (ddd, J = 17.1, 2.0, 1.2 Hz, 1 H), 5.62 (ddd, J = 17.2, 10.4, 8.3 Hz, 1 H). ^{13}C NMR: δ -5.2 (q, J = 119 Hz), 10.3 (t, J = 160 Hz), 18.4 (s), 19.7 (d, J = 157 Hz), 20.6 (d, J = 160 Hz), 25.9 (q, J = 123 Hz), 63.1 (t, J = 141 Hz), 114.4 (t, J = 156 Hz), 137.3 (d, J = 152 Hz). IR (neat): 3070, 3000, 2955, 2925, 2857, 1639, 1467, 1255, 1085, 840 cm^{-1}.

***cis*-2-(2′,2′-Dideuteriovinyl)-1-[(*tert*-butyldimethylsiloxy)methyl]cyclopropane (12).** This compound was made according to the procedure used to make the protio alkene except that tetrahydrofuran (170 mL), (methyl-d_3)triphenylphosphonium iodide (10.9 g, 26.7 mmol), *n*-BuLi in hexane (26.7 mmol), and **10** (5.00 g, 23.4 mmol) in 30 mL of tetrahydrofuran were used. **12** (4.51 g, 21.1 mmol, 90% yield) was recovered. ^{1}H NMR (361 MHz): δ 0.06 (s, 6 H), 0.43 (q, J = 5.4 Hz, 1 H), 0.91 (s, 9 H), 0.87–0.95 (m, 1 H), 1.22–1.31 (m, 1 H), 1.57–1.63 (m, 1 H), 3.54–3.70 (m, 2 H), 4.95–5.01 (m, 0.17 H), 5.07–5.15 (m, 0.17 H), 5.57–5.67 (m, 1 H).

***cis*-2-Vinylcyclopropanemethanol (13).** Compound **11** (2.96 g, 14.0 mmol), acetic acid (10.0 g, 0.17 mol), and water (10.0 g, 0.56 mol) were stirred for 9 h. This was added to an ice-cooled solution of 68 g of a 12% sodium hydroxide solution. Sodium chloride was added to saturate the aqueous solution, which was extracted with diethyl ether. After drying (MgSO$_4$) and removal of the bulk of the solvent, 4.54 g of solution remained. NMR indicated that the solution contained **13** (1.1 g, 11 mmol), *tert*-butyldimethylsilanol (1.5 g, 11 mmol), and diethyl ether (1.9 g). The products were separated via preparative GC by using a 5 ft × $^1/_4$ in. column packed with 20% Carbowax 20M on Chromosorb P 60/80 mesh. **13** (0.73 g, 7.4 mmol, 53% yield) was recovered. ^{1}H NMR (361 MHz): δ 0.48 (q, J = 5.4 Hz, 1 H), 0.97 (td, J = 8.2, 5.2 Hz), 1.28–1.46 (m, 1 H), 1.51–1.75 (m, 1 H), 3.47 (dd, J = 11.5, 8.9 Hz, 1 H), 3.78 (dd, J = 11.6, 6.3 Hz, 1 H), 5.06 (dd, J = 10.2, 1.4 Hz, 1 H), 5.20 (dm, major J = 17.0 Hz, 1 H), 5.65 (ddd, J = 17.0, 10.1, 8.6 Hz, 1 H).

***cis*-2-(2′,2′-Dideuteriovinyl)cyclopropanemethanol (14).** Compound **14** was prepared with the procedure used to make the protio compound expect that 3.90 g (18.2 mmol) of **12** was used. **14** (1.02 g, 10.2 mmol, 56% yield) was recovered. ^{1}H NMR (361 MHz): δ 0.48 (q, J = 5.4 Hz, 1 H), 0.97 (td, J = 8.2, 5.0 Hz, 1 H), 1.32–1.47 (m, 1 H), 1.61–1.71 (m, 1 H), 3.48 (dd, J = 11.6, 8.9 Hz, 1 H), 3.78 (dd, J = 11.6, 6.3 Hz, 1 H), 5.03–5.07 (m, 0.15 H), 5.15–5.23 (m, 0.15 H), 5.60–5.69, (m, 1 H).

***cis*-2-Vinylcyclopropanecarboxaldehyde (15).** To a solution of pyridine (9.5 g, 120 mmol) and methylene chloride (100 mL) was added chromium trioxide (6.0 g, 60 mmol). After 20 min, **13** (0.73 g, 7.4 mmol) in methylene chloride (20 mL) was added, and the mixture was stirred for 20 min. The solution was decanted from the residue, and the residue was washed with diethyl ether. The combined organic phases were washed with 5% sodium hydroxide, 5% hydrochloric acid, 10% sodium bicarbonate, and brine. After drying (MgSO$_4$), removal of solvent by distillation under N$_2$, and vacuum transfer, 1.2 g of colorless solution remained, which contained (by NMR integration) 0.43 g of **15**. Attempts to remove additional solvent by heating the pot with an 80 °C oil bath led to yellowing of the solution. After vacuum transfer, 0.90 g of liquid remained, which contained methylene chloride (420 mg), diethyl ether (86 mg), pyridine (40 mg), and the **15** (350 mg, 3.6 mmol, 49% yield). ^{1}H NMR (361 MHz): δ 1.43 (td, J = 8.0, 5.1 Hz, 1 H), 1.53 (dt, J = 6.8, 5.5 Hz), 2.16–2.23 (m, 2 H), 5.12 (d, J = 10.3 Hz, 1 H), 5.23–5.35 (d (J obscured by CH$_2$Cl$_2$), 1 H), 5.78 (ddd, J = 17.1, 10.2, 8.1 Hz, 1 H), 9.33 (d, J = 5.1 Hz, 1 H).[16]

***cis*-2-(2′,2′-Dideuteriovinyl)cyclopropanecarboxaldehyde (16).** The procedure used to make **16** was the same used to make **15** except that **14** (1.00 g, 10.0 mmol), chromium trioxide (8.0 g, 80 mmol), pyridine (12.6 g, 160 mmol), and methylene chloride (110 mL) were used and the oil bath used to distill off the solvents was never raised above 60 °C. Colorless liquid (1.36 g) was recovered containing **16** (0.71 g, 72 mmol, 72% yield), pyridine (0.13 g), methylene chloride (0.39 g), and diethyl ether (0.13 g). ^{1}H NMR of **16** (361 MHz): δ 1.42 (td, J = 8.0, 5.2 Hz, 1 H), 1.49–1.56 (m, 1 H), 2.04–2.15 (m, 2 H), 5.07–5.3 (m, integral value obscured by CH$_2$Cl$_2$), 5.73–5.81 (m, 1 H), 9.34 (d, J = 5.1 Hz, 1 H).

***cis*-1,2-Divinylcyclopropane (3).** The Wittig reagent was prepared by using the dimsyl anion as described by Corey.[17] A suspension of a 57% oil dispersion of sodium hydride (0.104 g, 2.5 mmol) and 7 mL of dry dimethyl sulfoxide was heated to 70–80 °C for 40 min. The resulting gray solution was cooled to room temperature, and methyltriphenylphosphonium bromide (0.94 g, 2.6 mmol) was added. The resulting red mixture was stirred for 20 min. The mixture was cooled to 18 °C, and a solution containing **15** (200 mg, 2.1 mmol), methylene chloride (240 mg), diethyl ether (49 mg), and pyridine (23 mg) was rapidly added via syringe. The mixture became dark red and was stirred for 30 s. A 0.3-Torr vacuum was applied for 1 min, and the product was collected in a liquid nitrogen cooled receiver that contained 1.5 mL of deuteriochloroform. The receiver was warmed to -60 °C under N$_2$. The solution was transferred via syringe to NMR tubes cooled to -78 °C. ^{1}H NMR data of **3** at 10 °C (361 MHz): δ 0.63–0.70 (m, 1 H), 1.05–1.18 (m, 1 H), 1.67–1.77 (m, 2 H), 5.00 (d, J = 10.3 Hz, 2 H), 5.14 (d, J = 17.2 Hz, 2 H), 5.48–5.60 (m, 2 H).

***cis*-1,2-Bis(2′,2′-dideuteriovinyl)cyclopropane (3d4).** The procedure to make **3d4** was the same as was used to make **3** except that a 57% oil dispersion of sodium hydride (122 mg, 2.9 mmol), dimethyl-d_6 sulfoxide (15 mL), (methyl-d_3)triphenylphosphonium iodide (1.26 g, 3.1 mmol), **16** (200 mg, 2.0 mmol), methylene chloride (110 mg), pyridine (37 mg), and diethyl ether (37 mg) were used. ^{1}H NMR data of **14** at 10 °C (361 MHz): δ 0.67 (apparent q, J = 5.5 Hz, 1 H), 1.13 (td, J = 8.1, 5.1 Hz, 1 H), 1.70–1.77 (m, 2 H), 4.97–5.15 (m, 0.28 H), 5.51–5.58 (br s, 2 H).

1,4-Cycloheptadiene (4). As peaks corresponding to diene **3** decreased in intensity in the NMR spectrum, a new set of peaks appeared, which correspond to the previously reported[3b] spectrum of **4**. ^{1}H NMR of **4** at 10 °C (361 MHz): δ 2.20–2.29 (br s, 4 H), 2.82–2.89 (br s, 2 H), 5.58–5.68 (m, 2 H), 5.73–5.83 (m, 2 H).

6,6,7,7-Tetradeuterio-1,4-cycloheptadiene (4d4). As peaks corresponding to diene **3d4** decreased in intensity in the NMR spectrum, a new set of peaks appeared. ^{1}H NMR of **4d4** at 10 °C (361 MHz): δ 2.20–2.26 (br s, 0.28 H), 2.86 (t, J = 4.9 Hz, 2 H), 5.61–5.68 (m, 2 H), 5.77 (br d, J = 11.1 Hz, 2 H). This corresponds to 93% deuterio incorporation. Samples from other preparations of **4d4** were found to contain 90% and 92% deuterium incorporation.

Modifications to the Nicolet 360 Spectrometer To Improve Temperature Control. The pyrometer in the probe of the NMR instrument which supplies information to the temperature controller had 1 °C sensitivity. It was replaced with Newport Electronics, Inc., Model No. 268-TC2 05,01,D3, which has 0.1 °C sensitivity. Appropriate software changes were also made.

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[16] For ^{1}H NMR data on **15**, see: Rhoads, S. J.; Cockroft, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 2815.

[17] Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128.

Table I

```
                              3 PROTIO RUN #1

PT #      INPUT t          INPUT A/Ao        RESIDUAL IN INPUT A/Ao

 1       .486090E+03      .566600E+00       .386371E-02
 2       .648120E+03      .517400E+00       .612109E-02
 3       .810150E+03      .470600E+00       .607314E-02
 4       .972180E+03      .415000E+00      -.704989E-02
 5       .113420E+04      .364100E+00      -.193593E-01
 6       .129620E+04      .337400E+00      -.110015E-01
 7       .178230E+04      .270300E+00       .900188E-02
 8       .194440E+04      .242200E+00       .480518E-02
 9       .210630E+04      .222400E+00       .669629E-02
1st order k (irrev.) =  .591840E-03  std. dev.:  .194024E-04
Intercept (-lnA/Ao)  =  .287257E+00  std. dev.:  .202212E-01
corr. coef.          =  .996260
```

```
                              3 PROTIO RUN #2

PT #      INPUT t          INPUT A/Ao        RESIDUAL IN INPUT A/Ao

 1       .486090E+03      .601700E+00      -.782972E-05
 2       .648120E+03      .547000E+00       .186661E-02
 3       .810150E+03      .490100E+00      -.377825E-02
 4       .972180E+03      .448800E+00       .135772E-02
 5       .113420E+04      .397900E+00      -.747483E-02
 6       .129620E+04      .372500E+00       .523306E-02
 7       .145830E+04      .338800E+00       .607884E-02
 8       .162030E+04      .303900E+00       .245681E-02
 9       .178230E+04      .278000E+00       .489444E-02
10       .194440E+04      .232700E+00      -.147168E-01
11       .210640E+04      .222000E+00      -.215797E-02
12       .226840E+04      .206900E+00       .381435E-02
1st order k (irrev.) =  .609402E-03  std. dev.:  .945899E-05
Intercept (-lnA/Ao)  =  .211759E+00  std. dev.:  .107667E-01
corr. coef.          =  .998798
```

```
                              3 PROTIO RUN #3

PT #     . INPUT t          INPUT A/Ao        RESIDUAL IN INPUT A/Ao

 1       .486090E+03      .627400E+00      -.147078E-02
 2       .648120E+03      .579300E+00       .461671E-02
 3       .810150E+03      .522000E+00      -.316493E-02
 4       .972180E+03      .475000E+00      -.491339E-02
 5       .113420E+04      .446400E+00       .783655E-02
 6       .129620E+04      .397300E+00      -.348073E-02
 7       .145830E+04      .365000E+00      -.123266E-02
 8       .162030E+04      .334200E+00      -.481318E-03
 9       .178230E+04      .308500E+00       .265184E-02
10       .194440E+04      .280600E+00       .111654E-02
11       .210630E+04      .256000E+00       .580142E-03
12       .226840E+04      .230200E+00      -.320218E-02
13       .243050E+04      .213800E+00       .517537E-03
1st order k (irrev.) =  .556111E-03  std. dev.:  .474697E-05
Intercept (-lnA/Ao)  =  .193509E+00  std. dev.:  .572949E-02
corr. coef.          =  .999599
```

```
                              3 PROTIO RUN #4

PT #      INPUT t          INPUT A/Ao        RESIDUAL IN INPUT A/Ao

 1       .477860E+03      .514200E+00       .550393E-02
 2       .629460E+03      .469400E+00       .326820E-03
 3       .781060E+03      .431900E+00      -.636560E-03
 4       .932660E+03      .397700E+00      -.114582E-02
 5       .108430E+04      .365200E+00      -.257141E-02
 6       .123590E+04      .331600E+00      -.752530E-02
 7       .138750E+04      .300500E+00      -.122105E-01
 8       .169070E+04      .277400E+00       .115070E-01
 9       .184230E+04      .249800E+00       .461772E-02
10       .199390E+04      .228300E+00       .221524E-02
11       .214550E+04      .207500E+00      -.974773E-03
1st order k (irrev.) =  .534907E-03  std. dev.:  .118064E-04
Intercept (-lnA/Ao)  =  .420294E+00  std. dev.:  .131538E-01
corr. coef.          =  .997815
```

```
PT #      INPUT t          INPUT A/Ao        RESIDUAL IN INPUT A/Ao

 1       .477860E+03      .683000E+00       .233351E-01
 2       .629460E+03      .614000E+00       .101259E-01
 3       .781060E+03      .546000E+00      -.680171E-02
 4       .932660E+03      .482000E+00      -.240488E-01
 5       .108430E+04      .449000E+00      -.142391E-01
 6       .123590E+04      .405000E+00      -.190609E-01
 7       .138750E+04      .369000E+00      -.191962E-01
 8       .169070E+04      .335000E+00       .969014E-02
 9       .184230E+04      .297000E+00      -.796935E-03
10       .199390E+04      .293000E+00       .203891E-01
11       .214550E+04      .257000E+00       .744503E-02
12       .229710E+04      .235000E+00       .655103E-02
13       .224870E+04      .223000E+00      -.119857E-01
14       .260030E+04      .206000E+00       .145589E-01
1st order k (irrev.) =  .582891E-03  std. dev.:  .183792E-04
Intercept (-lnA/Ao)  =  .137483E+00  std. dev.:  .222612E-01
corr. coef.          =  .994088
```

Table II

```
                              3D4 DEUTERIO RUN #1

PT #      INPUT t          INPUT A/Ao        RESIDUAL IN INPUT A/Ao

 1       .486090E+03      .576300E+00      -.811604E-02
 2       .648120E+03      .504800E+00      -.162816E-01
 3       .810150E+03      .487300E+00       .226891E-01
 4       .972180E+03      .426300E+00       .120400E-01
 5       .113420E+04      .374400E+00       .503168E-02
 6       .129620E+04      .329600E+00       .253936E-03
 7       .145830E+04      .278600E+00      -.150396E-01
 8       .162030E+04      .258500E+00      -.332276E-02
 9       .178230E+04      .234100E+00       .646584E-03
10       .194440E+04      .203200E+00      -.494324E-02
1st order k (irrev.) =  .707934E-03  std. dev.:  .255838E-04
Intercept (-lnA/Ao)  =  .193023E+00  std. dev.:  .260180E-01
corr. coef.          =  .994817
```

```
                              3D4 DEUTERIO RUN # 2

PT #     . INPUT t          INPUT A/Ao        RESIDUAL IN INPUT A/Ao

 1       .486090E+03      .523300E+00      -.242472E-02
 2       .648120E+03      .471000E+00       .622441E-02
 3       .810150E+03      .398000E+00      -.128925E-01
 4       .972180E+03      .370100E+00       .684371E-02
 5       .113420E+04      .326000E+00       .485486E-02
 6       .129620E+04      .288800E+00       .487987E-02
 7       .145830E+04      .245000E+00      -.599090E-02
 8       .162030E+04      .218400E+00      -.349770E-02
1st order k (irrev.) =  .760495E-03  std. dev.:  .217241E-04
Intercept (-lnA/Ao)  =  .273308E+00  std. dev.:  .199836E-01
corr. coef.          =  .997561
```

```
                              3D4 DEUTERIO RUN #3

PT #      INPUT t          INPUT A/Ao        RESIDUAL IN INPUT A/Ao

 1       .477860E+03      .535000E+00      -.427411E-02
 2       .629460E+03      .492000E+00       .739924E-02
 3       .781060E+03      .443000E+00       .752964E-02
 4       .932660E+03      .394000E+00       .267903E-02
 5       .108430E+04      .344000E+00      -.763766E-02
 6       .123590E+04      .303000E+00      -.129875E-01
 7       .138750E+04      .268000E+00      -.159517E-01
 8       .169070E+04      .238000E+00       .870560E-02
 9       .184230E+04      .218000E+00       .119522E-01
1st order k (irrev.) =  .705136E-03  std. dev.:  .256136E-04
Intercept (-lnA/Ao)  =  .280575E+00  std. dev.:  .244856E-01
corr. coef.          =  .995414
```

```
                              3D4 DEUTERIO RUN #4

PT #      INPUT t          INPUT A/Ao        RESIDUAL IN INPUT A/Ao

 1       .477860E+03      .554000E+00       .186815E-02
 2       .629460E+03      .499000E+00       .514283E-02
 3       .781060E+03      .441000E+00      -.733074E-03
 4       .932660E+03      .387000E+00      -.811041E-02
 5       .108430E+04      .348000E+00      -.539813E-02
 6       .123590E+04      .317000E+00       .901226E-03
 7       .138750E+04      .282000E+00      -.736169E-03
 8       .169070E+04      .225000E+00      -.120307E-02
 9       .184230E+04      .211000E+00       .867151E-02
1st order k (irrev.) =  .735756E-03  std. dev.:  .127498E-04
Intercept (-lnA/Ao)  =  .242380E+00  std. dev.:  .120731E-01
corr. coef.          =  .998951
```

Determination of Rate Constants for the Rearrangements of 3 and 3d4

The rates of rearrangement of **3** and **3d4**, its deuterated analogue, at 10 °C were obtained by determining the ratio of **3** or **3d4** and 1,4-cycloheptatrene as a function of time. This was done by integrating appropriate regions of a series of 361-MHz NMR spectra which were collected using the KINET program of the Nicolet 360 spectrometer. The mole fractions of **3** and **3d4** were determined by monitoring the decay of the syn hydrogen[3b] on carbon 3 (typically δ 0.55–0.80) of **3** or **3d4** and the growth of the two hydrogens on carbon 3 (typically δ 2.7–3.0) of 1,4-cycloheptatriene. The mole fractions of **3** and **3d4** were determined as follows:

$$\chi_{\mathbf{3}\mathrm{or}\mathbf{3d4}} = \frac{\text{integral for } \delta\ 0.55\text{–}0.80}{(\text{integral for } \delta\ 2.7\text{–}3.0)/2 + \text{integral for } \delta\ 0.55\text{–}0.80}$$

The internal clocks of the spectrometer do not take into account the time it takes to store each spectrum and to "zero the block"; therefore the times for spectral acquisition were determined by manually timing the events. The spectrometer began acquiring data approximately 1 min after the sample was introduced into the probe. The first two spectra of each run were discarded to allow the sample to warm to 10 °C. Spectra in which the χ of **3** or **3d4** was below 0.20 were discarded due to the difficulty of accurately integrating small peaks.

Acknowledgment. We thank the NSF for financial support of this work and R. Addleman (Indiana University) for modifications to the NMR spectrometer.

Appendix. See Tables I and II.

Registry No. 1, 16177-46-1; **3**, 2984-58-9; **3d4**, 124200-42-6; **4**, 7161-35-5; **4d4**, 124200-43-7; *cis*-**5**, 826-34-6; *trans*-**5**, 826-35-7; *cis*-**6**, 2345-68-8; *trans*-**6**, 2345-75-7; **7**, 124200-36-8; **9**, 124200-37-9; **10**, 124200-38-0; **11**, 124200-39-1; **12**, 124200-44-8; **13**, 15135-97-4; **14**, 124200-40-4; **15**, 22823-00-3; **16**, 124200-41-5; methyl acrylate, 96-33-3; methyl chloroacetate, 96-34-4; cyclohexanone, 108-94-1; pyridinium chlorochromate, 26299-14-9; deuterium, 7782-39-0.

Thermochemical Studies of Carbonyl Reactions. 4. Enthalpies of Hydrolysis of Norbornyl Ketals

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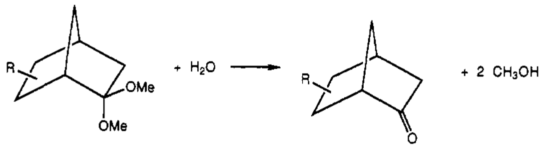
The dimethyl ketals of norbornanone and of eight methyl-substituted norbornanones were prepared, and the enthalpies of hydrolysis were determined. The compounds were chosen to provide a variety of steric interactions between the methyl substituents and the ketal group, much of which would be relieved on going to the ketone. The enthalpies of reaction varied by over 4 kcal/mol. The experimental data were modeled by molecular mechanics (MM2), and although a good correlation was found for the less substituted compounds, the ketal of camphor fell off the slope = 1 correlation line. The free energy changes were determined, and were found not to be well correlated with the enthalpy changes.

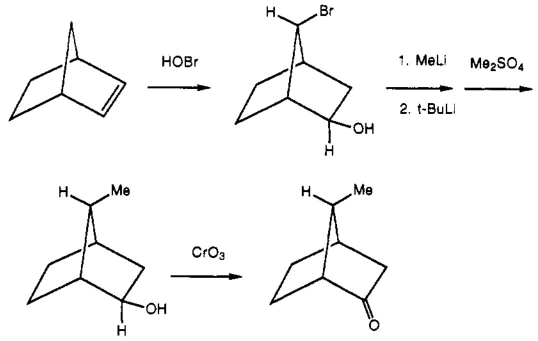
Steric effects are commonly associated with the conversion of a trigonal carbon to tetrahedral, as in ester hydrolysis,[1] semicarbazone formation,[2] and a wide variety of related processes. The free energies of activation for many of these reactions may be satisfactorily correlated with Taft's E_s values.[3] In order to gain further information concerning the origin of steric effects, we have measured via calorimetry the effect of alkyl substituents on the difference in energy between aldehydes and acetals,[4] ketones and ketals,[5] and esters and orthoesters.[6] Here, the enthalpy changes did not correlate with the free energy changes, and for the smaller alkyl groups, entropy changes were the dominant component of the free energy terms.

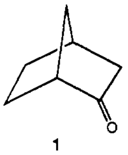
The conformational freedom characteristic of these open-chain compounds makes it difficult to study them via semiempirical methods such as molecular mechanics.[7] Therefore, we have now examined the heats of hydrolysis of methyl-substituted 2,2-dimethoxynorbornanes. Here, it is possible to introduce one or more methyl groups in different orientations with regard to the ketal function. The ring system is relatively rigid, and the use of methyl groups minimizes conformational problems.



The ketones were obtained from commercial sources (**1**, **9**), prepared via literature procedures or modifications thereof (**2**, **3**, **4**, **5**, **8**), or prepared via a procedure developed in this work (Scheme I, **6**). All of the ketones were

Scheme I





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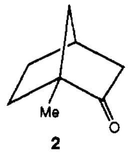

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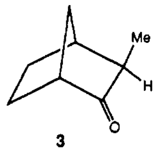

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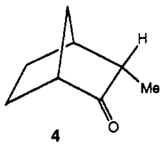

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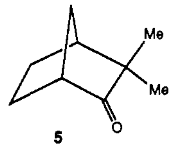

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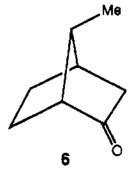

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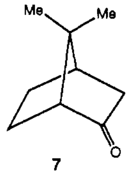

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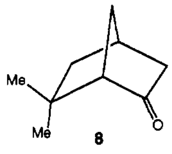

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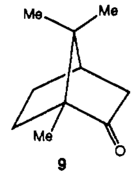

9

carefully purified and converted to their dimethyl ketals using methyl orthoformate. This reaction proceeded well

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