Stereochemistry of the Thermal Conversion of 1-Vinyl-2,3-cisdideuteriocyclobutane to Butadiene and 1,2-Dideuterioethylenes

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Abstract. This study has examined the stereochemistry of the decomposition at 900–1000 K in a single-pulse shock tube of 1-vinyl-2,3-*cis*-dideuteriocyclobutane to ethylenes and buta-1,3-dienes. The deuterated ethylenes formed during the decomposition, CHD=CH₂, (*E*)-CHD=CHD, and (*Z*)-CHD=CHD, were quantified via two independent techniques, FTIR and IR absorption spectroscopy using a tunable diode laser spectrometer. The results of both analyses indicated that equal amounts of (*E*)-CHD=CHD and (*Z*)-CHD=CHD were formed from the cis-labeled reactant. In an earlier shock tube study of the decomposition at 1000–1200 K of two deuterium-labeled cyclohexenes to ethylenes plus buta-1,3-dienes, a pathway via a vinylcyclobutane intermediate was implicated in a significant fraction of the decomposition events; the measured ratios of (*E*)-CHD=CHD to (*Z*)-CHD=CHD in that study were consistent with a complex mechanistic model in which the stereochemistry of deuterium labels in the cyclohexene reactant was lost in ethylene products formed via vinylcyclobutane. The present results provide additional support for that model.

INTRODUCTION

The mechanistic alternatives for bimolecular Diels– Alder cycloadditions of dienes with dienophiles and the corresponding retroadditions, the unimolecular conversion of cyclohexenes to butadienes and ethylenes, have attracted sustained theoretical and experimental attention over many decades as applications of both Diels– Alder cycloaddition and cýcloreversion processes in synthetic work have multiplied beyond counting.¹

Numerous kinetic studies on the thermal reaction of cyclohexene (1) to form butadiene (2) and ethylene (3) have provided activation parameters for this prototypical instance of the retroaddition, and recent experimental work on the thermal retroadditions of deuterium-labeled cyclohexenes has demonstrated that they form butadiene and ethylene with less than complete stereospecificity.² The data obtained agreed well with the kinetic model outlined in Scheme 1 involving four unimolecular rate constants and vinylcyclobutane (4) as an intermediate.

The four rate constants of Scheme 1 and the rate constant k_5 for thermal isomerization of one isomer of CHD=CHD to the other as functions of temperature made possible calculations providing the expected pro-



Scheme 1

portions of alternative ethylenic products formed from the deuterium-labeled cyclohexenes $1-d_4$ and $1-d_6$ at any temperature. The experimentally determined amounts of CH₂=CD₂ derived from $1-d_4$ (relative to CH₂=CH₂),

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and of (*E*)-CHD=CHD, (E)-3-d₂ from $1-d_6$ (relative to (*Z*)-CHD=CHD (*Z*)-3-d₂) were found to be in good agreement with the kinetic model of Scheme 1, provided that CHD=CHD formed from $1-d_6$ by way of the vinylcyclobutane intermediate $4-d_6$ gave equal proportions of (*E*) and (*Z*) isomers.

The present work addressed the stereochemistry of the vinylcyclobutane \rightarrow butadiene + ethylene reaction, one of the two steps which, according to the kinetic model and the experimental stereochemical results ob-



tained for the cycloreversion of $1-d_6$, might occur with some or complete loss of stereochemical integrity. A vinylcyclobutane system having deuterium labels at C2 and C3 in a well-defined cis disposition was prepared and decomposed in single-pulse shock tube experiments. The relative amounts of (*E*) and (*Z*) isomers of CHD=CHD were then determined through FTIR and tunable diode laser (TDL) infrared spectroscopic analyses. The reaction, it was found, gives equal amounts of both isomers of CHD=CHD.

Synthesis of the deuterium-labeled vinylcyclobutane $4-d_2$ was accomplished through the reaction sequence outlined in Scheme 2. The key step involved reduction of olefin 7 with dideuteriodiimide³ in CH₃OD: two



deuteriums were thus added cis to one another, giving a mixture of syn and anti versions of alcohol 8.

EXPERIMENTAL

General

The instrumentation used and general experimental conventions followed in the synthesis of $4-d_2$ are recorded in ref 4.

Cyclobut-2-enemethanol (7) was prepared through a fivestep route (Scheme 2). Free radical chlorination of 1,1cyclobutanedicarboxylic acid (Aldrich) at C3 with sulfuryl chloride and benzoyl peroxide in benzene followed by hydrolysis and thermal carboxylation provided a mixture of the two 3-chlorocyclobutanecarboxylic acids (5).5 These acids were converted to the related acid chlorides with thionyl chloride, and the mixture of acid chlorides was reduced with LiAlH₄ in ether-THF at -20 °C to give the 3-chlorocyclobutanemethanols (6). Finally, dehydrochlorination with potassium tert-butoxide in DMSO afforded the known unsaturated alcohol 7.6 A sample purified by preparative GC on a 1-m 17% Carbowax 20M column exhibited 'H NMR absorptions in accord with expectations: δ 1.4 (br s, 1H), 2.3 (d, 1H, J = 13.6 Hz), 2.6 (dd, 1H, J = 0.7, 13.6 Hz), 3.1 (q, 1H, 0.7 Hz), 3.7 (d, 2H, J = 6.2 Hz, 6.1 (d, 1H, 2.9 Hz) 6.2 (d, 1H, J = 2.9 Hz); MS m/z 84 (M⁺, 100), 47 (47), 35 (70).

cis-2,3-Dideuteriocyclobutanemethanol (8). To a solution of alcohol 7 (410 mg, 4.9 mmol) dissolved in 5 mL of CH₃OD (99 atom% D) was added 2 g of dipotassium azodicarboxylate; the reaction mixture was stirred as 1.4 mL (25 mmol) of CD₃COOD (99.9 atom% D) was added dropwise over 1 h. Water was added, and the product was extracted with 3×25 mL CH₂Cl₂. The combined extracts were dried and concen-



Scheme 2

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trated by distillation using a 15-cm Vigreux column to give 430 mg of crude product 8. The ¹H NMR spectrum of a sample purified by preparative GC on a 1-m XF-1150 column had absorptions at δ 1.53 (s, 1H), 1.9 (br m, 4H), 2.5 (quintet, 1H, J = 7.2 Hz), and 3.6 (m, 2H).

1-Vinyl-cis-2,3-dideuteriocyclobutane (4-d2). Oxidation of 430 mg of crude alcohol 8 with 2.1 g (9.8 mmol) of PCC in dry CH₂Cl₂, followed by a standard workup, gave 360 mg of crude cis-2,3-dideuteriocyclobutanecarboxyaldehyde: MS m/z 86 $(M^+, 8)$, 57 (100). The Wittig reagent prepared from methyltriphenylphosphonium bromide and NaH (10 mmol each) in freshly distilled DMSO was combined with this aldehyde (360 mg, 4.2 mmol) at 0 °C. The hydrocarbon product was collected in a trap at -78 °C as the reaction mixture was warmed to 70 °C and a slight flow of N2 was maintained. The product 4-d₂ and authentic vinylcyclobutane-d₀ (from cyclobutanemethanol (Aldrich) via the aldehyde and a Wittig reaction) showed identical GC retention times on two capillary columns; the d_2 -hydrocarbon had MS m/z 69 (10), 68 (9), 67 (4), 55 (82), 54 (100); ¹H NMR δ 5.9 (ddd, 1H, J = 3.6, 8.5, 17 Hz), 4.9 (m, 2H), 2.9 (m, 1H), 2.1 (m, 2H), 1.9 (m, 2H); ¹³C NMR δ 143.3, 111.8, 39.0, 28.2, 18.4; for authentic vinylcyclobutane-d₀ (compare ref 7) : MS m/z 67 (11), 54 (100); ¹H NMR δ 5.9 (ddd, 1H, J = 3.6, 8.5, 17 Hz), 4.9 (m, 2H), 2.9 (m, 1H), 2.1 (m, 2H), 1.9 (m, 4H); ¹³C NMR δ 143.3, 111.8, 39.1, 28.2, 18.4.

Thermal Reactions and Analyses of Products

The decomposition of the deuterium-labeled vinylcyclobutane 4-d₂ was studied in a 2.54-cm-diameter glass single-pulse shock tube having a high-temperature residence time of 8×10^{-4} s at the downstream end; the instrument and operating procedures have been described previously.2.8 Reactant samples were prepared on a high-vacuum line and stored in 1-L glass bulbs equipped with greaseless stopcocks; glass beads were added to the flasks to permit rapid mixing by gentle swirling. Appropriate experimental conditions for the study were determined by shock-heating a 1.0%-in-argon sample of unlabeled 4; then two experiments were run on an identically prepared 1.0%-in-argon mixture of 4-d2. Immediately following each shock, a 50-cm³ sample (A) was withdrawn for GC analysis, followed by a 200-cm³ sample (B) for spectroscopic analysis. Extents of conversion to 1, 2, and 3 were determined via GC analysis (sample A) on a Varian 1440-20 chromatograph equipped with a H₂ flame ionization detector and a 2-m × 3.2-mm polypropylene glycol/silver nitrate column. Calibrations were performed using authentic samples of unlabeled 1, 2, 3, and 4, diluted in argon. From the extent of decomposition of 4 in each experiment, the reaction temperature was calculated assuming irreversible first-order kinetics, using the activation parameters $\log_{10}(A, s^{-1}) = 14.5$, $E_a = 49.3$ kcal/mol.⁹ The argon diluent was removed from each B sample by evaporation at 77 K (liquid N₂ bath); then the sample was warmed to 143 K (pentane slush bath) to release the ethylenes, which were retained for spectroscopic analysis.

The ratio of (E)-3-d₂ to (Z)-3-d₂ in the ethylene fraction was determined first via FTIR (Nicolet 760); absorbances of Q-branch features at 987.7 and 842.4 cm⁻¹, respectively, were

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compared with calibration curves produced from a 1.05/1.00 (*E*)-**3**-d₂/(*Z*)-**3**-d₂ mixture prepared from samples supplied by Merck, Sharpe and Dohme.¹⁰ The *E*/*Z* concentration ratio was also measured via IR absorption at 913 cm⁻¹ using an ultrahigh resolution TDL spectrometer, described previously;^{2,11} concentrations of **3**-d₁ and **3**-d₀ were also measured (see ref 2 for description of **3**-d₁ synthesis).

RESULTS

Table 1 presents the results of the two shock tube (ST) experiments. The FTIR (a) and (b) results stem from analyses of the ethylenes from shock tube experiment #1 on two days, two months apart; standard series were run on each occasion. For the TDL analyses, (a) and (b) denote two different pairs of closely adjacent (E)-3-d₂ and (Z)-3-d₂ absorption features of similar intensities that lie at different settings of the TDL spectrometer.

From the TDL analyses, the concentration ratios $3 \cdot d_1/3 \cdot d_2$ and $3 \cdot d_0/3 \cdot d_2$ averaged $1.49(\pm .09)$ and $0.43(\pm .04)$, respectively; these correspond to product ethylene percentages of $3 \cdot d_0 = 14.7(\pm 1.5)\%$, $3 \cdot d_1 = 51.1(\pm 3.1)\%$, and $3 \cdot d_2 = 34.2(\pm 1.4)\%$.

DISCUSSION

During the earlier study of the pyrolysis of $1-d_6$, a brief study of the isomerization rate of $3-d_2$ was run in the same shock tube used in the present study.² Measurable ethylene isomerization was observed during the 8×10^{-4} reaction time only at temperatures above 1100 K. Thus, the CHD=CHD isomers formed from $4-d_2$ in the present study should not have equilibrated after formation to any appreciable extent.

The uncertainties in the measurement of (E)-3-d₂ and (Z)-3-d₂ features in the FTIR spectra were estimated at $\pm 2\%$, leading to an uncertainty in the E/Z ratio of $\pm .04$. The major source of error is assignment of the baseline, which has a gradual slope due to many unresolved weak absorption features of these and the other ethylene isotopomers. Thus, the agreement between FTIR data points (a) and (b) in Table 1 is better than would be expected with a large number of data points. In contrast, the extremely high resolution $(1 \times 10^{-5} \text{ cm}^{-1})$ of the TDL

Table 1. Summary of (E)-CHD=CHD/(Z)-CHD=CHD ratios measured in reaction products

Expt	<i>T</i> (K)	Reactant consumed	$\frac{(E)-3-\mathbf{d}_2}{(Z)-3-\mathbf{d}_2}$	Analysis method
ST-1	963	80.1%	1.00 1.01	FTIR(a) FTIR(b)
ST-2	945	63.4%	1.00 1.01 0.93	TDL (a) TDL (a) TDL (b)

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spectrometer allows complete separation of adjacent vibration-rotation features, so that the estimated errors in absorption measurements and E/Z ratios are $\pm 1\%$ and ± 0.02 , respectively. There is, however, a possible source of systematic error in the TDL analysis: the laser may be emitting, and the optics capturing, more than one wavelength of light (multi-mode oscillation). To guard against this, the laser beam is passed through a 2 cm⁻¹-bandpass monochrometer and examined for mode purity with a germanium etalon, and the calibration curves are examined for deviations from Beer's Law behavior; however, a slight contribution of a second mode at a particular laser setting might escape notice, leading perhaps to the E/Z ratio reported as TDL (b) for ST-2 in Table 1. Taken together, however, the data give convincing evidence of the virtually complete loss of stereochemistry in the ethylenes produced by fragmentation of $4-d_2$.

The initial chlorination reaction (forming 8 in Scheme 2) was not quantitative; some unreacted diacid remained. Decarboxylation then gave some cyclobutanecarboxylic acid along with 5 and, through incomplete purification of intermediate compounds, 8d_o along with 8, and finally unlabeled vinylcyclobutane in the gas-chromatographically-purified labeled substrate $4-d_2$. This d₀-component, about 10% of the sample, and the inevitable C2 and C3 monodeuteriumlabeled analogs, about 10% of each, were irrelevant to the stereochemical distinction to be made between Eand Z isomers of 1,2-d2-ethylene, but they did of course contribute to the observed distribution of d_0 , d_1 , and d_2 . ethylenes formed. Neglecting possible secondary deuterium kinetic isotope effects at the temperatures of the shock tube experiments, one would expect from these isotopomers a d₀:d₁:d₂ ethylene product mixture of 15:50:35, in complete agreement with the proportions observed after thermal reactions by TDL infrared spectroscopic analyses.

The mass spectral base peaks at m/z 57 and 58 for the fragment ions CH₂=CH–CH=OH⁺ and CHD=CH– CH=OH⁺ derived from alcohol **8** and its isotopic variants provided other evidence qualitatively consistent with this distribution of labels: the 57:58 peak intensities observed, 100:71, and the ratio determined for an authentic sample of **8**-d₀, 100:15, led to an inferred ratio of CH₂=CH–CH=OH⁺ to CHD=CH–CH=OH⁺ fragment ions of 100:56, or 64:36. A 10:10:10:70 distribution of d₀-, C2-d₁-, C3-d₁-, and C2,C3-*cis*-d₂- versions of cyclobutanemethanol would be expected to give these ions in a 60:40 ratio. The relative intensities of m/z 54 and 55 ions shown by **4**-d₂ (see Experimental) gave a similar internal check reasonably consistent with the other measures of label distribution.

CONCLUSIONS

The concerted cycloreversions of 1, $1-d_4$, and $1-d_6$, which take place with preservation of stereochemical relationships, are kinetically dominant, but the diradicalmediated processes outlined in Scheme 3 for d_0 -structures also contribute significantly to the observed chemistry.

Thermal cleavage of the C1–C2 bond of vinylcyclobutane 4 may give rise to two diradicals, having either Z or E stereochemistry at C3. The first of these allylic-alkanyl diradicals, (Z)-9, might form cyclohexene or fragment to give butadiene and ethylene or reclose to 4. The second, (E)-9, could fragment to 2 plus 3 or cyclize to vinylcyclobutane. Either diradical species could well have sufficient conformational flexibility and lifetime to permit partial or complete scrambling of the stereochemistry of CHD at the primary alkanyl radical center, C6. Partial loss of stereochemistry was previously observed in the fragmentation of deuterated cyclobutane.¹² The present work demonstrates complete loss of stereochemistry for the fragmentation of $4-d_2$.



Scheme 3

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