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Thermal Isomerization of (3-Butenyl)cyclopropane to Norbornane

John E. Baldwin,* Richard C. Burrell, and Rajesh Shukla

Department of Chemistry, Syracuse University, Syracuse, New York 13244

jbaldwin@syr.edu

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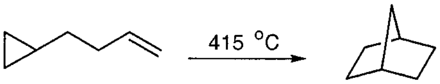
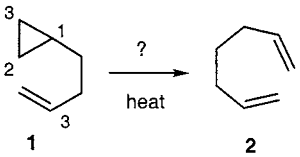
ABSTRACT



(3-Butenyl)cyclopropane isomerizes thermally to norbornane and gives rise to many other products. Deuterium and carbon-13-labeled versions of (3-butenyl)cyclopropane have been prepared and isomerized, establishing that the formation of norbornane involves cleavage of the cyclopropyl C2−C3 bond.

(3-Butenyl)cyclopropane (**1**) has been prepared,[1,2] but the thermal chemistry of this hydrocarbon has apparently not been investigated. It constitutes the simplest system having the structural characteristics appropriate to a Cope-like rearrangement involving one double bond and one cyclopropane moiety. Whether it might rearrange to 1,6-heptadiene (**2**) was the question instigating the present work (Scheme 1).

Scheme 1



Were **1** to behave like a simple alkyl-substituted cyclopropane, cyclopropane-to-propene isomerizations giving diene **2**, the (*E*)- and (*Z*)-isomers of 1,5-heptadiene, and 2-methyl-1,5-hexadiene would be expected to occur at 415 °C with a rate constant of about 7×10^{-6} s^{-1}.[3] A distinction between the Cope-like process and the cyclopropane-to-propene alternative leading from **1** to diene **2** might be attained through carbon-13-labeling experiments.

The thermal chemistry of 1,6-heptadiene itself has been studied in some detail. It reacts primarily through a retro-ene fragmentation to form 1,3-butadiene and propene; the Arrhenius parameters are $\log(k, s^{-1}) = 11.3$ and $E_a = 47.0$ kcal/mol.[4,5] Reaction mixtures at relatively high conversions, analyzed by GC with 1/4-in. packed columns and TC detectors, included the secondary products 4-methylcyclohexene and toluene and many others to lesser extents: methane, ethylene, 1-butene, butane, cyclopentene, 1,3-cyclohexadiene, benzene, cycloheptene, and some minor unidentified impurities.[4]

In a test run diene **2** was heated in the gas phase with pentane as a bath gas at 415 °C for 16 h. The complex product mixture was examined by capillary GC and GC/MS, with tentative structural assignments based on comparisons with authentic samples and spectral libraries. The C6 to C8 products included hexane, hexenes, methylcyclopentenes, cyclohexane, cyclohexadienes, benzene, cyclohexene, methylcyclohexane, 4-methylcyclohexene, toluene, 1-methylcyclohexene, cycloheptene, ethylcyclohexene, ethylbenzene, xylenes, and several minor unidentified products.

Diels−Alder additions of the initially formed 1,3-butadiene and propylene, followed by inter- and intramolecular hydrogen transfers and [1,5] shifts, can account for most of

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[1] Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256−4264.

[2] Kirmse, W.; Grassmann, D. *Chem. Ber.* **1966**, *99*, 1746−1763.

[3] (a) Setser, D. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1964**, *86*, 564−569. (b) Halberstadt, M. L.; Chesick, J. P. *J. Phys. Chem.* **1965**, *69*, 429−438.

[4] Egger, K. W.; Vitins, P. *J. Am. Chem. Soc.* **1974**, *96*, 2714−2719.

[5] King, K. D. *J. Phys. Chem.* **1980**, *84*, 2517−2521.

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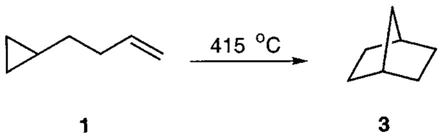
these secondary products. Cycloheptene probably forms from **2** through an intramolecular ene reaction.[6]

(3-Butenyl)cyclopropane[7] (**1**) was heated in a static reactor[8] at 415 °C with pentane as a bath gas and cyclooctane as a standard. A complex mixture of products was formed, one similar to the mixture derived from diene **2**. It contained unchanged **1**, some 4-methylcyclohexene, 1-methylcyclohexene, and toluene, and various amounts of hexane, ethylcyclopropane, hexenes, methylcyclopentenes, cyclohexane, cyclohexadienes, benzene, cyclohexene, methylcyclohexane, dimethylcyclopentenes, ethylcyclohexene, ethylbenzene, xylenes, and several very minor unidentified products. Most surprisingly, a saturated isomeric product was also formed: it was isolated, characterized, and proved to be norbornane (**3**) (Scheme 2). A product mixture after 24 h at 415 °C contained 8% of **3** along with 1-methylcyclohexene (10%), unchanged **1** (15%), 4-methylcyclohexene (16%), and toluene (22%).

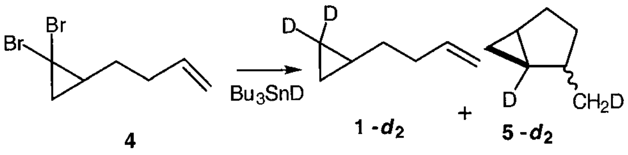
Scheme 2



The initial rate of isomerization of **1** was about 4 × 10^{-5} s^{-1}, some 6-times faster than expected for cyclopropane-to-propylene isomerizations. The complicated kinetic situation was not pursued as the isomerization of **1** to **3** was examined in greater detail.

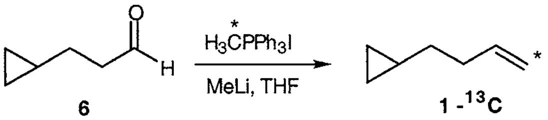
The topology of the isomerization of **1** to **3** was defined with the aid of isotopically labeled analogues of the substrate. Dibromocarbene and 1,5-hexadiene gave a monoadduct (**4**),[9−11] which was reduced with tributyltin deuteride[12,13] to afford **1**-d_2[14] (Scheme 3). Careful purification by preparative GC separated it completely from the isomeric coproducts, the exo and endo forms of **5**-d_2.[10,15]

Scheme 3



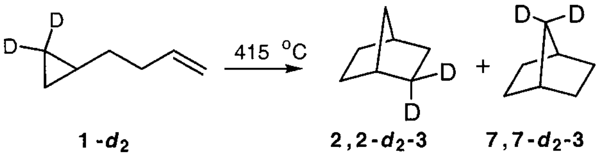
A carbon-13-labeled version of **1** was secured from cyclopropanepropanal[16] (**6**) through a Wittig condensation with (^{13}C-methylene)triphenylphosphorane (Scheme 4). Aldehyde **6** was prepared through two routes, one featuring a classic malonic ester alkylation with bromomethylcyclopropane[17] (commercial cyclopropanemethanol/PBr$_3$; NaH/diethyl malonate; aqueous NaOH; heat; LAH/THF; PCC) and the second based on the reaction of cyclopropyllithium with trimethylene oxide,[18] followed by oxidation of cyclopropanepropanol with PCC.

Scheme 4



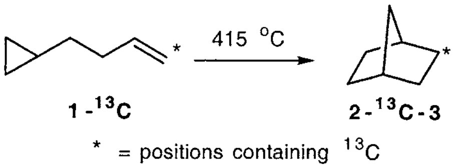
The thermal isomerization of **1**-d_2 gave d_2-norbornanes that exhibited two broad singlets in the deuterium NMR spectrum, at δ 1.47 and 1.19, in a relative intensity ratio of 1:3. This spectrum is indicative of the product being a 1:1 mixture of 2,2-d_2-norbornane and 7,7-d_2-norbornane (Scheme 5). The unlabeled hydrocarbon shows a proton NMR spectrum having three multiplets, at δ 2.2 (bridgehead H), 1.47 (endo methylene H), and 1.19 (exo and C7 methylene H) in 2:4:6 proportions.[19]

Scheme 5



When **1**-^{13}C was isomerized to norbornane, the label was found exclusively at C2. The ^{13}C-spectrum showed but one signal, at δ 29.7[19,20] (Scheme 6).

Scheme 6



The NMR spectra of samples of 4-methylcyclohexene and toluene recovered from isomerizations of **1**-d_2 and **1**-^{13}C had

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[6] Kalra, B. L.; Afriyie, Y.; Brandt, B.; Lewis, D. K.; Baldwin, J. E. *J. Phys. Chem.* **1995**, *99*, 8142−8146.

[7] Hydrocarbon **1**: ^{1}H NMR δ 5.86 (ddt, J = 17.3, 10.4, 6.6 Hz, 1 H), 5.06−4.88 (m, 2 H), 2.21−2.08 (m, 2 H), 1.29 (dt, J = 7.7, 6.9 Hz, 2 H), 0.77−0.61 (m, 1 H), 0.45−0.36 (m, 2 H), 0.06−0.03 (m, 2 H); ^{13}C NMR δ 139.1, 114.1, 34.2, 33.9, 10.6, 4.4; MS m/z (rel intensity) 95 (1), 81, (34), 68, (29), 67 (59), 55 (100), 54 (46), 41 (26), 39 (73).

[8] (a) Baldwin, J. E.; Bonacorsi, S. J.; Burrell, R. C. *J. Org. Chem.* **1998**, *63*, 4721−4725. (b) Baldwin, J. E.; Burrell, R. C. *J. Org. Chem.* **1999**, *64*, 3567−3571.

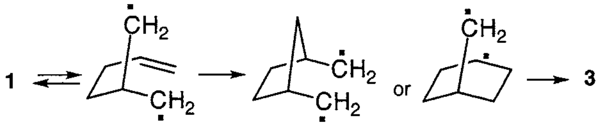
[9] Skattebøl, L. *J. Org. Chem.* **1964**, *29*, 2951−2956.

[10] Descoins, C.; Julia, M.; van Sang, H. *Bull. Soc. Chim. Fr.* **1971**, *17*, 4087−4093.

labels at all possible positions. The extensive scrambling was particularly apparent for the products from **1**-^{13}C: 4-methylcyclohexene-^{13}C had resonances at ^{13}C NMR δ 126.8, 126.7, 33.7, 30.8, 28.3, 25.3, 22.0;[19] the toluene sample showed absorptions at δ 137.9, 129.0, 128.2, 125.3, 21.4 ppm.[21] These indications of complex secondary reactions contrast sharply with the highly specific labeling observed for **3**-d_2 and **3**-^{13}C products.

The labeling results of Schemes 5 and 6 are consistent with a reaction topology involving cleavage of the C2−C3 bond of the cyclopropane substructure of the reactant and formation of new bonds between these two carbon atoms and the olefinic carbon atoms of the butenyl moiety. A plausible mechanistic hypothesis (Scheme 7) might involve initial generation of a 2-substituted trimethylene diradical (**7**), isomerization through formation of a new carbon−carbon bond to give a 1,5-diradical, **8** or **9**, and rapid formation of a second new C−C bond.

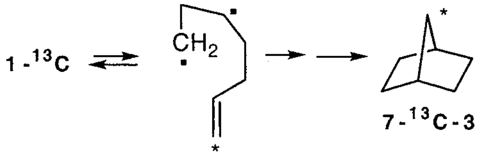
Scheme 7



7 **8** **9**

The deuterium and carbon-13 outcomes are clearly inconsistent with formation of norbornane through cleavage of C1−C2 of the cyclopropane unit. Were that to occur, followed by formation of a 1,5-diradical on the way to product, the norbornane obtained would have deuterium only at C2 and carbon-13 only at C7. The carbon-13 case is outlined in Scheme 8.

Scheme 8



Thermal additions of two ethylenic components to give cyclobutanes are well-known,[22] but the isomerization of **1** to **3** may be the first recorded instance of an intramolecular thermal rearrangement of a simple hydrocarbon leading from a cyclopropane plus ethylene combination to a cyclopentane product. It could well take place through the steps outlined formally in Scheme 7. The generality of this type of conversion and the reliability of this mechanistic suggestion remain to be uncovered.

Acknowledgment. We thank the National Science Foundation for support of this work through CHE-9902184.

Supporting Information Available: ^{1}H, ^{2}H, and ^{13}C NMR spectra for key synthetic intermediates, **1**, **1**-d_2, and **1**-^{13}C and for major thermal isomerization products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) **1**-d_2: ^{1}H NMR (cyclopropyl protons) δ 0.77−0.61 (m, 1 H), 0.43−0.34 (m, 1.04 H), 0.04−0.03 (m, 1.04 H).

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(16) Aldehyde **6**: ^{1}H NMR δ 9.80 (t, J = 1.9 Hz, 1 H), 2.54 (td, J = 7.1, 1.9 Hz, 2 H), 1.59−1.48 (m, 2 H), 0.79−0.63 (m, 1 H), 0.50−0.41 (m, 2 H), 0.09−0.01 (m, 2 H); ^{13}C NMR δ 202.9, 44.1, 27.4, 10.5, 4.7; MS *m/z* (rel intensity) 98 (1, M^{+}), 97 (4), 83 (19), 69 (43), 55 (60), 54 (79), 42 (60), 41 (100), 39 (100).

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(19) Pouchert, C. J.; Behnke, J. *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, 1st ed.; Aldrich: Milwaukee, WI, 1993; Vol. 1, pp 54, 59, 60.

(20) (a) Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107−7120. (b) Stothers, J. B.; Tan, C. T.; Teo, K. C. *Can. J. Chem.* **1973**, *51*, 2893−2901.

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