(d, J = 4.3 Hz, 1 H), 4.95 (m, 2 H), 4.75 (br t, 1 H), 4.56 (d, J = 5.2 Hz, 1 H), 4.42 (m, 2 H), 4.21 (d, J = 7.7 Hz, 1 H), 4.17 (d, J = 5.8 Hz, 1 H), 3.75–3.5 (m, ~6 H), 3.35–3.2 (m, ~3 H), 3.2–3.05 (m, 2 H), 3.05–2.9 (m, 2 H). ^{13}C NMR (DMSO-d_6): δ 103.21 (d, J = 159 Hz, anomeric C(1')), 78.50 (d, J = 139 Hz, glycosidic C(3)), 76.80 (d, J = 141.5), 76.49 (d, J = 142 Hz), 73.63 (d, J = 145 Hz), 70.85 (d, J = 143 Hz), 70.66 (d, J = 144 Hz), 69.82 (d, J = 142.5 Hz), 62.44 (t, J = 139 Hz), 61.86 (t, J = 140.5 Hz), 61.50 (t, J = 141.5 Hz). Anal. Calcd for $C_{11}H_{22}O_{10}\cdot H_2O$: C, 39.76; H, 7.29. Found: C, 39.50; H, 7.03.

3-*O*-β-D-Galactopyranosyl-D-arabinitol. ^{1}H NMR (DMSO-d_6) [peaks broadened due to partial OH exchange]: δ 5.06 (br s, 1 H), ~4.65 (br m, 3 H), ~4.35 (br m, 3 H), 4.16 (d, J = 6.8 Hz, 1 H, anomeric CH), ~4.15 (br s, 1 H), 3.75–3.4 (m, ~9 H), 3.4–3.2 (m, ~4 H). ^{13}C NMR (DMSO-d_6): δ 104.04 (d, J = 159 Hz, anomeric C(1')), 79.30 (d, J = 140.5 Hz, glycosidic C(3)), 75.22 (d, J = 134 Hz), 73.45 (d, J = 136 Hz), 70.89 (d, J ~ 144.5 Hz, 2 C (coincidental overlap)), 70.17 (d, J = 140 Hz), 68.25 (d, J = 142 Hz), 62.50 (t, J = 139 Hz), 61.80 (t, J = 142.5 Hz), 60.75 (t, J ~ 140 Hz). Anal. Calcd for $C_{11}H_{22}O_{10}\cdot 0.5H_2O$: C, 40.86; H, 7.18. Found: C, 40.66; H, 6.92.

5-*O*-α-D-Galactopyranosyl-D-arabinitol. ^{1}H NMR (DMSO-d_6) [peaks slightly broadened due to incipient OH exchange]: δ 4.63 (d, J ~ 2.2 Hz, 1 H), 4.56–4.44 (m, 4 H), 4.38–4.33 (m, 2 H), 4.20 (d, J = 6.3 Hz, 1 H), 4.13–4.06 (m, ~1 H), 3.75–3.3 (m, ~12 H), 3.15 (d, J = 4.8 Hz, 1 H). ^{13}C NMR (DMSO-d_6): δ 99.06 (d, J = 167.1 Hz, anomeric C), 70.95 (d, J ~ 140 Hz), 70.28 (d, J = 136.5 Hz), 69.8 (d, J ~ 141 Hz, 2 C (coincidental overlap)), 69.8 (t, J ~ 142 Hz, glycosidic C(5)), 69.13 (d, J ~ 138 Hz), 68.9 (d, J ~ 143 Hz), 68.8 (d, J ~ 143 Hz), 62.88 (t, J = 139 Hz), 60.48 (t, J = 139.5 Hz). Anal. Calcd for $C_{11}H_{22}O_{10}\cdot 0.5H_2O$: C, 40.86; H, 7.18. Found: C, 40.84; H, 7.26.

5-*O*-β-D-Glucopyranosyl-D-arabinitol. ^{1}H NMR (DMSO-d_6) [peaks slightly broadened due to incipient OH exchange]: δ 5.1–4.9 (m, 3 H), 4.6–4.4 (m, 3 H), 4.3–4.1 (m, 3 H), 4.03 (d, J = 9.7 Hz, 1 H), 3.75–3.55 (m, 3 H), 3.5–3.25 (m, 5 H), 3.2–2.9 (m, 5 H). ^{13}C NMR (DMSO-d_6): δ 103.74 (d, J = 161 Hz, anomeric C), 76.84 (d, J = 140 Hz), 76.33 (d, J = 139.5 Hz), 73.70 (d, J ~ 144 Hz), 72.68 (t, J ~ 144 Hz, glycosidic C(5)), 70.43 (d, J = 138 Hz), 70.01 (d, J ~ 140 Hz, 69.91 (d, J = 138 Hz), 62.89 (t, J ~ 142 Hz), 60.96 (t, J ~ 142 Hz). Anal. Calcd for $C_{11}H_{22}O_{10}\cdot 0.5H_2O$: C, 40.86; H, 7.18. Found: C, 40.89; H, 7.31.

2-*O*-β-D-Galactopyranosylerythritol.[61] ^{1}H NMR (DMSO-d_6) [peaks broadened due to partial OH exchange]: δ 5.00 (br d, 1 H), 4.73 (br d, 1 H), 4.60 (br s, 1 H), 4.58 (d, J = 6 Hz, 1 H), 4.41 (d, J = 4 Hz, 2 H), 4.20–4.14 (br m, 2 H), 3.7–3.2 (m, ~12 H). ^{13}C NMR (DMSO-d_6): δ 104.10 (d, J = 156 Hz, anomeric C(1')), 83.06 (d, J = 141 Hz, glycosidic C(2)), 75.27 (d, J = 138 Hz), 73.26 (d, J = 137 Hz), 71.19 (d, J = 140 Hz, 70.84 (d, J ~ 147 Hz), 68.13 (d, J = 142 Hz), 62.84 (t, J = 140 Hz), 61.91 (t, J = 142 Hz), 60.40 (t, J = 143 Hz).

Acknowledgment. We would like to thank Dr. Morris Bullock for helpful discussions and Elinor Norton for GC–MS analyses. This work was carried out at Brookhaven National Laboratory under contract De-AC02-76CH00016 with the United States Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Registry No. 1, 14694-95-2; 3, 53716-93-1; $RuCl_2(PPh_3)_3$, 15529-49-4; $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)_2]^+(BF_4)^-$, 70196-21-3; D-glucose, 50-99-7; D-arabinitol, 488-82-4; D-arabinose, 10323-20-3; erythritol, 149-32-6; 2-deoxy-D-*arabino*-hexose, 154-17-6; 1-deoxy-D-arabinitol, 13942-77-3; *N*-acetyl-D-glucosamine, 7512-17-6; 1-(acetylamino)-1-deoxy-D-arabinitol, 92283-19-7; D-melibiose, 585-99-9; 5-*o*-α-D-galactopyranosyl-D-arabinitol, 122741-76-8; glyceraldehyde, 367-47-5; 2-deoxy-D-ribose, 533-67-5; D-glucoheptose, 3146-50-7; D-glucitol, 50-70-4; ribitol, 488-81-3; D-allose, 2595-97-3; D-xylose, 58-86-6; D-threitol, 2418-52-2; D-erythrose, 583-50-6; glycerol, 56-81-5; DL-glyceraldehyde, 56-82-6; ethylene glycol, 107-21-1; glycolaldehyde, 141-46-8; methanol, 67-56-1; D-fucose, 3615-37-0; 2-deoxy-D-allose, 6605-21-6; 1-deoxy-D-ribitol, 13046-76-9; 2-deoxy-D-galactose, 1949-89-9; 5-deoxy-D-arabinitol, 67968-44-9; L-rhamnose, 3615-41-6; 5-deoxy-L-arabinitol, 97466-38-1; 6-deoxy-D-glucose, 7658-08-4; 1-deoxy-D-erythritol, 4144-94-9; *N*-acetyl-D-mannosamine, 3615-17-6; *N*-acetyl-D-galactosamine, 1811-31-0; 5-(acetylamino)-5-deoxy-D-arabinitol, 122741-77-9; 2-(acetylamino)-2-deoxy-D-galactonolactone, 24960-16-5; 2-deoxy-2-fluoro-D-glucose, 29702-43-0; 1-deoxy-1-fluoro-D-arabinitol, 122741-78-0; D-maltose, 69-79-4; 3-*O*-α-D-glucopyranosyl-D-arabinitol, 122795-46-4; cellobiose, 528-50-7; 3-*O*-β-D-glucopyranosyl-D-arabinitol, 122795-47-5; D-lactose, 63-42-3; gentiobiose, 554-91-6; 5-*O*-β-D-glucopyranosyl-D-arabinitol, 122741-79-1; 3-*O*-β-D-galactopyranosyl-D-arabinose, 6057-48-3; 2-*O*-β-D-galactopyranosylerythritol, 14955-25-0.

Supplementary Material Available: Additional experimental details and spectroscopic data (10 pages). Ordering information is given on any current masthead page.

Stereochemistry of the Diels–Alder Reaction of Butadiene with Cyclopropene

John E. Baldwin* and V. Prakash Reddy

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

Received April 24, 1989

1(*E*)-Deuteriobutadiene and cyclopropene react at 0 °C to give 2-*endo*-deuteriobicyclo[4.1.0]hept-3-ene; 1-(*Z*)-deuteriobutadiene leads to the 2-*exo*-deuterio bicyclic product. Analysis of these products through ^{2}H NMR spectroscopy reveals complete stereospecificity, indicating that the transition structure having an endo orientation of diene and cyclopropene is strongly favored over the alternative exo geometry.

Introduction

The [2 + 4] cycloaddition of butadiene with ethylene is the prototypical Diels–Alder reaction, the one most readily studied through calculational methods.[1-3] The reaction of butadiene with cyclopropene[4] is the simplest Diels–Alder combination of hydrocarbons for which an

(1) Schoeller, W. W. *J. Org. Chem.* **1980**, *45*, 2161–2165, ref 19.
(2) Burke, L. A. *Theoret. Chim. Acta* **1985**, *68*, 101–105. Burke, L. A. *Int. J. Quantum Chem.* **1986**, *29*, 511–518.
(3) Houk, K. N.; Lin, Y.-T.; Brown, F. K. *J. Am. Chem. Soc.* **1986**, *108*, 554–556. Brown, F. K.; Houk, K. N.; Burnell, D. J.; Valenta, Z. *J. Org. Chem.* **1987**, *52*, 3050–3059. Loncharich, R. J.; Brown, F. K.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 1129–1134.
(4) Wiberg, K. B.; Barley, W. J. *J. Am. Chem. Soc.* **1960**, *82*, 6375–6380.

0022-3263/89/1954-5264$01.50/0

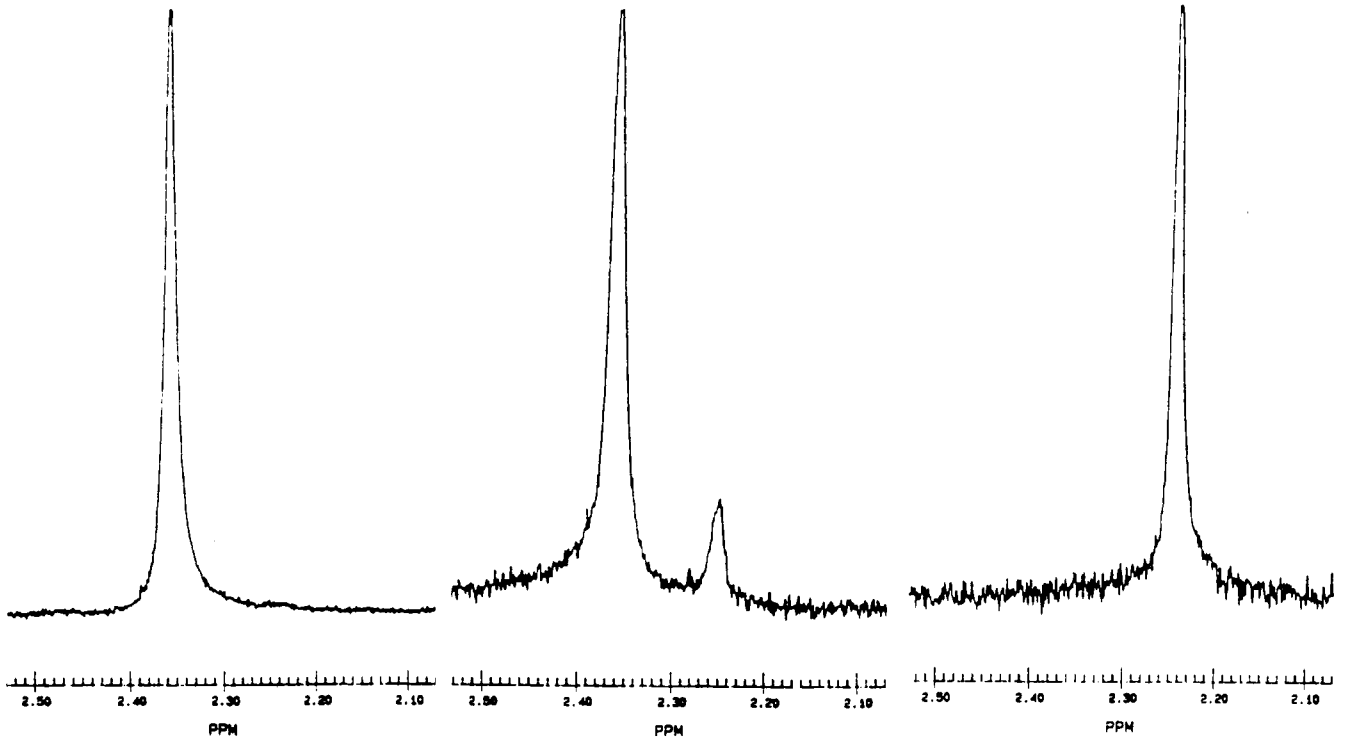
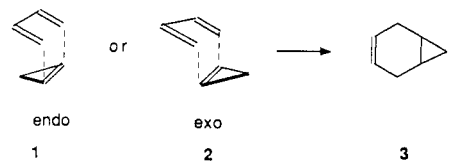


Figure 1. ^2H NMR spectra at 76.8 Mz for Diels–Alder adducts from cyclopropene and butadienes **5** (left) and **4** (right); the middle spectrum is for a mixture of these adducts in a 5:4 82:18 ratio.

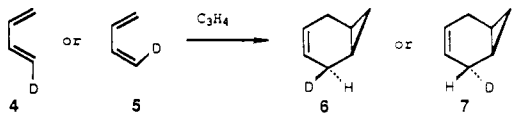
endo versus exo stereochemical issue must be considered; either an endo orientation of reactants (**1**) or an exo transition state structure (**2**) might lead to the cycloaddition product, bicyclo[4.1.0]hept-3-ene (**3**).



This point has been recognized for more than 20 years,[5] but it has not been subjected to direct experimental investigation. Attempts to clarify the issue have been predicated on theoretical considerations and calculations for **1** and **2**,[6] or on experimental studies of similar reactions shown by substituted butadienes and cyclopropenes.[7-9] The former favor **1** over **2**; experimental evidence derived from studies of a variety of substituted cases is still inconclusive.[9]

Even when a substituted instance of the reaction between butadiene and cyclopropene has been well defined stereochemically, there remain intrinsic problems of extrapolation between theory and experiment. For example, GAUSSIAN 82 ab initio 6-31G*//3-21G calculations on the alternative transition structures **1** and **2** predict that **1** is 2.8 kcal/mol more stable than **2**.[6] The reaction between 1(*E*)-methoxybutadiene and cyclopropene gives 2-*endo*-methoxybicyclo[4.1.0]hept-3-ene, a stereochemical assignment based on the absence of a H2–H7 NOE; less than 1% of the C2 epimeric product is formed.[9] The two indications of preferred transition structure geometry certainly agree, but cannot be compared without some uncertainty. Does the methoxy substituent merely serve as a stereochemical marker, or does it influence the stereoselectivity of the reaction?

To establish the preferred transition structure for the Diels–Alder reaction of butadiene with cyclopropene, we have prepared stereospecifically deuterium-labeled butadienes **4** and **5**, combined them with cyclopropene, and defined reaction stereochemistry through quantitative analysis of the products **6** and **7**.



Such an approach has been applied to the reaction between butadiene and maleic anhydride,[10] another Diels–Alder reaction for which the endo versus exo stereochemical issue in the absence of a label is not reflected in the product.

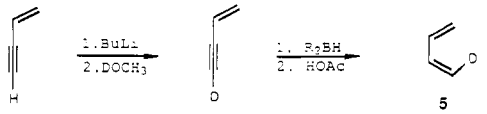
Results

Labeled dienes **4** and **5** were prepared with high deuterium incorporation and stereospecificity from vinylacetylene.[11,12] Reaction of this enyne with disiamylborane, followed by *O*-deuterioacetic acid, gave diene **4**.[13] Deprotonation of vinylacetylene in THF solution at −78 °C

(5) Herndon, W. C.; Hall, L. H. *Tetrahedron Lett.* **1967**, 3095–3100.
(6) Apeloig, Y.; Arad, D. 9th IUPAC Conference on Physical Organic Chemistry, Regensbury, FRG; August 23, 1988.
(7) Deem, M. L. *Synthesis* **1972**, 675–691.
(8) Plemenkov, V. V.; Breus, V. A. *J. Org. Chem. U.S.S.R.* **1974**, *10*, 1672–1674. Plemenkov, V. V.; Breus, V. A.; Grechkin, A. N.; Novikova, L. K. *J. Org. Chem. U.S.S.R.* **1976**, *12*, 787–791. Plemenkov, V. V.; Grechkin, A. N.; Novikova, L. K. Lecture, *3rd Conf Stereochem. Conform. Anal. Org. Petrochem. Synth.* **1976**, 7–8; *Chem. Abstr.* **1978**, *89*, 23617h.
(9) Apeloig, Y.; Arad, D.; Kapon, M.; Wallerstein, M. *Tetrahedron Lett.* **1987**, *28*, 5917–5920.
(10) Stephenson, L. M.; Smith, D. E.; Current, S. P. *J. Org. Chem.* **1982**, *47*, 4170–4171. See also: Stephenson, L. M.; Gemmer, R. V.; Current, S. *J. Am. Chem. Soc.* **1975**, *97*, 5909–5910.
(11) Mirakyan, S. M.; Davtyan, N. M.; Arakelyan, E. M.; Chukhadzhyan, G. A. *Arm. Khim. Zh.* **1982**, *35*, 201–202; *Chem. Abstr.* **1982**, *97*, 55237r.
(12) Dehmlow, E. V.; Lissel, M. *Synthesis* **1979**, 272–274.
(13) Baldwin, J. E.; Reddy, V. P.; Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 8554 and references therein.

4

with butyllithium, followed by reaction with methanol-*d*, gave 1-deuteriobut-3-en-1-yne; reduction of the triple bond using disiamylborane and then acetic acid provided diene **5**.



5

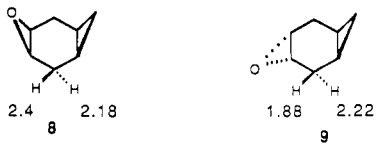
Proton NMR integrations of dienes **4** and **5** showed 99% and 98% incorporation of deuterium at the anticipated positions. The ^2H NMR spectra for **4** and **5** established stereochemical homogeneity: there was no deuterium absorption for the other labeled diene in either preparation, and **4** was not contaminated with 2-deuteriobutadiene. Reaction of dienes **4** or **5** with cyclopropene[14] at 0 °C gave 2-deuteriobicyclo[4.1.0]hept-3-enes with very high stereospecificity. When **4** was the reactant, the deuterium in the product was evident at δ 2.25; the deuterium in the bicycloheptene product derived from diene **5** was observed at δ 2.36 (Figure 1). In neither case was a deuterium NMR absorption for the other product detected. The two resonance signals are fully resolved; solutions containing samples of adducts from both cycloadditions show both absorptions distinctly (Figure 1). The Diels–Alder reaction then is completely stereospecific, within the experimental uncertainties of the ^2H NMR analytical method employed.

Tentative assignments of stereochemistry for C2 and C5 protons in bicyclo[4.1.0]hept-3-ene were derived through chemical shift comparisons with related cyclopropane-fused bicyclic compounds; such systems typically have endo-C2-H absorptions at higher field than those for exo-C2-H, a result of some shielding by the proximal three-membered ring.[15,16] Hence the deuterium label at δ 2.24 may be assigned as endo and the one at δ 2.38 as exo.

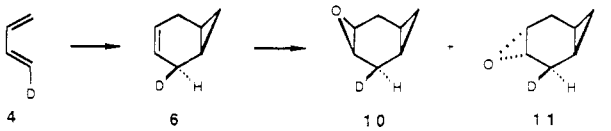
Attempts to check this tentative assignment based on other NMR techniques were not decisive. Proton decoupling experiments and 2D double quantum filtered COSY spectra showed a coupling of the C2–C5 protons at δ 2.38 and the bridgehead protons at δ 0.96 with a coupling constant of 2 Hz. This fact, however, seemed insufficient for an unambiguous assignment, since bicycloheptene can adopt two nearly isoenergetic conformations, and geometrical relationships for bridgehead and endo and exo C2–C5 protons vary significantly from one conformer to the other.

Sure stereochemical assignments for the 2-deuteriobicyclo[4.1.0]hept-3-enes were made by converting them to the corresponding epoxides.[17,18] Assignments for the C2–H NMR absorptions in the unlabeled *cis*- and *trans*-3,4-epoxybicyclo[4.1.0]heptanes have been determined with the aid of $Eu(dpm)_3$ shift reagent studies; the relative chemical shifts of protons at C2 in CCl_4 are dominated by stereochemical relationships with respect to the oxygen functionality, as shown in **8** and **9**.[17]

The adduct derived from diene **4** in $CDCl_3$ showed relative proton absorption intensities of 1:2 at δ 2.42:2.20–2.25 in the cis epoxide and of 2:1 at δ 2.26–2.34:1.89 in the trans epoxide. Thus the deuterium label is cis to the cyclopropane ring, and **4** gives **6**, which in turn leads to **10** and **11**.



8 9



4 6 10 11

Conclusions

The stereochemistry of the Diels–Alder reaction between butadiene and cyclopropene is now defined experimentally; this stereochemically cryptic reaction has been rendered easily perceived by employing stereochemically well-defined deuterium-labeled reactants. The stereochemical preference for the endo transition state **1**, as anticipated by Herndon and Hall,[5] and projected from ab initio calculations by Apeloig and Arad[6] to be about 99.4:0.6 at 0 °C, is confirmed.

This preference for an endo transition-state structure seems well rationalized through recognizing the inherent geometrically conditioned differences in primary overlap relationships for **1** and **2**.[5,6] The possible importance of other factors contributing to overall endo versus exo stereochemical preferences in Diels–Alder reactions of larger substituted reactants still merits careful consideration: secondary orbital overlap interactions, steric effects, and dipole–diple or other electrostatic contributions may in some instances play an influential role. But for the simplest possible Diels–Alder reaction of hydrocarbon reactants for which the endo versus exo issue is relevant, a reaction for which reaction stereochemistry cannot be conditioned by the "maximum accumulation of unsaturation" consideration, both experiment and theory agree: the endo orientation is heavily favored.

Experimental Section

Diethyl ether was distilled from sodium benzophenone ketyl immediately before use. All reactions were carried out under a nitrogen atmosphere. Proton NMR spectra were recorded for $CDCl_3$ solutions at 300 MHz on a GE QE 300 spectrometer. Deuterium NMR spectra were obtained for CCl_4 solutions at 76.8 MHz on a GE GN 500 spectrometer. Chemical shifts (δ) are expressed relative to internal Me_4Si (0.0 ppm) in ^1H NMR and $CDCl_3$ (7.26 ppm) in ^2H NMR spectra.

Analytical gas chromatographic analyses were carried out with a 0.2-mm i.d. 25-m cross-linked 5% phenyl methyl silicone fused silica capillary column and a 0.2-mm i.d. 25-m methyl silicone capillary column, a HP 5780 instrument with flame-ionization detectors, and HP 3390A and 3392A reporting integrators. Preparative gas chromatographic separations were performed with a Varian A-90-P3 instrument using the following columns: A, SE-30 on Chromosorb W 60/80 (0.6 cm × 3.6 m); B, 10% dibutyl tetrachlorophthalate (DBTCP) on Chromosorb W 60/80 (0.6 cm × 2.5 m), connected to a 0.6 cm × 35 cm column of 10% SE-30 on Chromosorb W.[19] Compounds isolated by preparative GC were better than 98% homogeneous as judged by analytical GC; structural assignments were confirmed through NMR comparisons with the known undeuteriated analogues.

3-Buten-1-yne.[11,12] To excess potassium hydroxide (95 g) dissolved in 100 mL of water, 1 g of benzylhexadecyldimethyl-

(14) Closs, G. L.; Krantz, K. D. *J. Org. Chem.* **1966**, *31*, 638.
(15) Renaud, P.; Fox, M. A. *J. Org. Chem.* **1988**, *53*, 3745–3752.
(16) Grimme, W.; Doering, W. V. E. *Chem. Ber.* **1973**, *106*, 1765–1780.
(17) Aumelas, A.; Casadevall, E.; Casadevall, A. *Tetrahedron* **1978**, *34*, 2481–2490.
(18) Banwell, M. G.; Halton, B. *Aust. J. Chem.* **1980**, *33*, 2277–2290.
(19) Baldwin, J. E.; Broline, B. M. *J. Am. Chem. Soc.* **1982**, *104*, 2857–2865.

ammonium chloride, and dimethyl sulfoxide (60 mL) was added 1,4-dichloro-2-butene (35 g, 0.28 mol) dropwise over a 30-min period at a rate causing the reaction solution to reflux gently. After the addition was complete and the exothermicity of the reaction had subsided, the reaction mixture was heated to 90–110 °C for 1 h. The condensate in the trap was distilled to give pure 3-buten-1-yne (10 g, 69%): ^{1}H NMR δ 2.91 (d, 1.4 Hz, C1-H), 5.54–5.58 (m, 1 H), 5.75–5.78 (m, 2 H).

[1-^{2}H]But-3-en-1-yne. To but-3-en-1-yne (vinylacetylene; 7 g, 0.13 mol) dissolved in 100 mL of dry THF cooled to −78 °C was added dropwise with stirring *n*-butyllithium (53 mL of 2.5 M solution in hexanes, 0.13 mol). An orange solution formed at the end of the addition. After the addition, the reaction mixture was stirred for another 15 min at −78 °C. The reflux condenser was attached through an exit tube to a receiver flask cooled to −78 °C. Methanol-*d* (99.5 atm % d, 4.3 g, 5.2 mL, 1 equiv) was added. When the precipitates became colorless, the reaction mixture was warmed to room temperature and stirred for 30 min. The receiver flask was found to contain *n*-butane and [1-^{2}H]-but-3-en-1-yne in about a 1:1 ratio. A ^{1}H NMR examination of the product mixture indicated 99% deuteriation at C1.

(1*E*)-[1-^{2}H]-1,3-Butadiene (4). 2-Methyl-2-butene (18.2 g, 27.5 mL, 0.26 mol) was added to a flask cooled to 0 °C. Dry THF (50 mL) was added, and borane–dimethyl sulfide (13 mL of 10 M solution, 0.13 mol) was injected into the flask slowly. After the addition, the reaction mixture was stirred for 1 h at 0 °C. The resulting disiamylborane was added to an ice-cold solution of vinylacetylene (6.8 g, 0.13 mol) in 10 mL of dry THF; the reaction mixture was stirred for 15 min at 0 °C. Dimethyl sulfide was removed under vacuum. The reaction flask was connected to a receiver flask cooled to −78 °C through an exit tube attached to a reflux condenser, and acetic acid-*d* (98 atm % d, 10 mL, 0.17 mol, 1.3 equiv) was slowly injected into the flask at 0 °C. The quenched reaction mixture was then warmed to 60 °C and stirred for 1 h. A ^{1}H NMR analysis of the contents of the receiver flask revealed the presence of 1(*E*)-deuteriobutadiene, contaminated with trace amounts of dimethyl sulfide: ^{1}H NMR δ 5.11 (d, 1 H, J = 9.2 Hz, C4-*E*-H), 5.21 (dd, 2 H, J = 4.4, 15.8 Hz, C1, C4-*Z*-H), 6.31–6.42 (m, 2 H, C2, C3-H); ^{2}H NMR δ 5.12. There were no signals at δ 5.22 or 6.42 corresponding to the 1(*Z*)- or 2-deuteriobutadienes.

(1*Z*)-[1-^{2}H]-1,3-Butadiene (5). Using a similar procedure, 5 g (0.094 mol) of [1-^{2}H]but-3-en-1-yne was reacted with disiamylborane and then excess acetic acid to furnish the 1(*Z*)-deuteriobutadiene: ^{1}H NMR δ 5.07–5.14 (2 H, C1, C4-*E*-H), 5.18–5.26 (1 H, C4-*Z*-H), 6.30–6.41 (m, 2 H, C3, C4-H). Integration of the proton NMR signals showed 99% deuteriation. ^{2}H NMR δ 5.22. There was no signal at δ 5.12 corresponding to the 1*E* isomeric product.

Cyclopropene was prepared from 3-chloropropene following a standard procedure.[14] The cyclopropene was collected in an efficient receiver flask cooled with a dry ice–acetone bath: ^{1}H NMR δ 0.94 (t, 2 H, J = 1.4 Hz, C3-H), 7.09 (t, 2 H, J = 1.3 Hz, C2, C3-H). The proton NMR also showed 3-chloropropene as a contaminant.

Reaction of Butadienes with Cyclopropene. Butadiene, or one of the labeled butadienes **4** or **5** (0.5 g, 9 mmol), was added to excess cyclopropene (obtained from 15 g of 3-chloropropene) at 0 °C. After 2 h, NMR analysis of the reaction mixture showed the complete disappearance of the butadiene. The product bicyclo[4.1.0]hept-3-ene was purified by GC on column A, at a column temperature of 100 °C (retention time = 4 min).

Bicyclo[4.1.0]hept-3-ene.[4] ^{1}H NMR δ 0.29 (dd, 1 H, J = 5.1, 9.3 Hz, C7-endo-H), 0.45–0.52 (m, 1 H, C7-exo-H), 0.93–0.99 (m, 2 H, C1, C6-H), 2.24 (d, 2 H, J = 20 Hz, C2, C5-cis-H), 2.38 (d, 2 H, J = 20 Hz, C2, C5-trans-H), 5.44 (d, 2 H, J = 2.5 Hz, C3, C4-H).

***endo*-[2-^{2}H]Bicyclo[4.1.0]hept-3-ene (6) from 4:** ^{2}H NMR δ 2.25 ppm. There was no absorption at δ 2.36 characteristic of the C2 epimeric product.

***exo*-[2-^{2}H]Bicyclo[4.1.0]hept-3-ene (7) from 5:** ^{2}H NMR δ 2.36 ppm. There was no absorption at δ 2.25 characteristic of the C2 epimeric product (Figure 1).

[2-^{2}H]-3,4-Epoxybicyclo[4.1.0]heptanes.[17,18] The deuterium-labeled bicyclo[4.1.0]hept-3-ene **6** (100 mg, 1.1 mmol) from the reaction of butadiene **4** with cyclopropene was dissolved in 10 mL of dichloromethane, and excess *m*-chloroperoxybenzoic acid (1.5 g of 50–60% pure material, 4 to 5 mmol) was added. The reaction mixture was stirred at room temperature for 1 h. A capillary GC analysis showed complete disappearance of the olefin and formation of the cis and trans epoxides in a 4:6 ratio. The reaction mixture was then washed with 50 mL of saturated sodium sulfite and 50 mL of saturated sodium bicarbonate. The combined organic layers were dried (MgSO4) and filtered; the filtrate was concentrated and the product was purified by preparative GC using column B at a column temperature of 85 °C. The retention times of the cis and trans epoxides under these conditions were 9 and 10.5 min, respectively.

Cis epoxide 10: ^{1}H NMR δ 0.32 (1 H, apparent dt, J = 3.7, 9.2 Hz, C7-cis-H), 0.58 (apparent q, J = 3.97 Hz, C7-trans-H), 0.73–0.79 (2 H, C1, C6-H), 2.20–2.25 (br d, 2 H, C2, C5-trans-H), 2.42 (d, 1 H, J = 15.95 Hz, C2, C5-cis-H), 3.05 (s, 2 H, C3, C4-H).

Trans epoxide 11: ^{1}H NMR δ −0.38 to −0.34 (m, 1 H, C7-cis-H), 0.68–0.79 (m, 3 H, C7-trans-H, C1, C6-H), 1.89 (d, 1 H, J = 15.75 Hz, C2, C5-H, cis to cyclopropane), 2.26–2.34 (br m, 2 H, C2, C5-H, trans to cyclopropane), 3.01 (s, 2 H, C3, C4-H).

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged. We thank Professor Yitzhak Apeloig of the Israel Institute of Technology, Haifa, for encouragement and helpful correspondence.

Supplementary Material Available: NMR spectra for 3–11 (4 pages). Ordering information is given on any current masthead page.