the conductivity plots have previously been shown to be in excellent agreement with those based upon emf measurements using ion-selective electrodes.[27] Furthermore, SDS behaves as a typical 1:1 electrolyte below its cmc.[28]

Pseudo-first-order rate constants (k_{obsd}) for the neutral hydrolysis of 1 were reproducible to within 2%. The rate constants reported in Tables II-V have been determined for each series with the same surfactant stock solution to which varying amounts of polymer and/or salt were added. This procedure was employed to avoid ambiguities that may result from factors such as aging of the surfactant solution. Several control experiments were run using SDS-PEO and SDS-PPO solutions prepared from the same SDS stock solution. The latter data showed the same trends in k_{obsd} as found previously.

Acknowledgment. The investigations were supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. SDS, 151-21-3; CTAB, 57-09-0; PEO, 25322-68-3; PPO, 25322-69-4; 1-benzoyl-3-phenyl-1,2,4-triazole, 79746-00-2.

(27) Zana, R. *J. Colloid Interface Sci.* **1980**, *78*, 330.
(28) (a) Cutler, S. G.; Meares, P. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1758. (b) Parfitt, G. D.; Smith, A. L. *J. Phys. Chem.* **1982**, *86*, 942.

Specifically Deuteriated Bicyclo[3.2.0]hepta-2,6-dienes

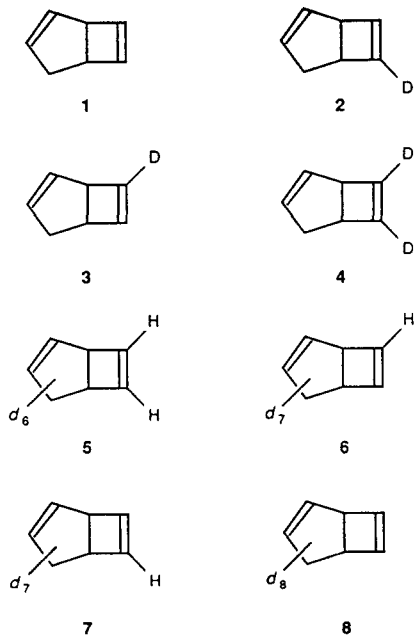
John E. Baldwin* and Kevin D. Belfield

Department of Chemistry, Syracuse University, Syracuse, New York 13244-1200

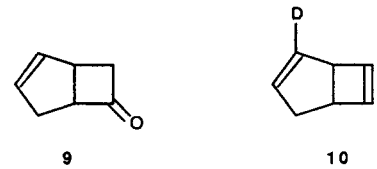
Received May 1, 1987

An efficient synthetic route from the dichloroketene/cyclopentadiene adduct to bicyclo[3.2.0]hepta-2,6-diene has been developed and adapted to prepare deuteriated analogues of this diene labeled specifically at C1-C5, C6, or C7, or any combination of these possibilities.

Bicyclo[3.2.0]hepta-2,6-diene (1) and specifically deuteriated analogues such as **2-8** were required in fair quantities for studies of several stereochemical and mechanistic problems. A perusal of the literature provided little encouragement that established synthetic routes could be exploited.



Relatively small quantities of the unlabled diene 1 may be secured through photochemical isomerization of cycloheptа-1,3,5-triene,[1-4] but the conversion lacks efficiency, does not lend itself to convenient scale-up, and cannot be adapted to secure specifically deuteriated variants. Synthesis of diene 1 from bicyclo[3.2.0]hept-2-en-6-one (**9**), an intermediate readily accessible through the cycloaddition of cyclopentadiene with ketene[5] or dichloroketene,[6-8] has attracted attention for more than 30 years, yet the overall conversion of **9** → **1** has been achieved only in disappointing yields.

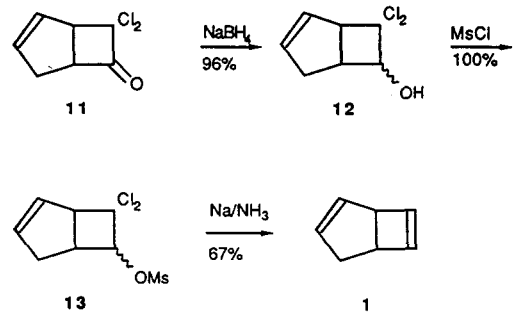


Hofmann degradation of the trimethylammonium hydroxide derived from **9** by way of the oxime and the 6-amino bicyclic olefin achieved the first synthesis of **1**, in very low yield.[9] Reduction of ketone **9** gives predominantly the endo alcohol; mesylate, tosylate, and methyl xanthate derivatives of the alcohol react solvolytically or thermally to give mostly cyclohepta-1,3,5-triene.[10-12] Assisted ionization of these derivatives with cleavage of the C1-C5 bond appears stereoelectronically favorable.[13] A synthesis of **2** from **9** by $LiAlD_4$ reduction and pyrolysis of the mixture of xanthates did give the specifically labeled product, but after isolation and purification by preparative gas chromatography, the overall yield for **9** → **2** was only

(1) Dauben, W. G.; Cargill, R. L. *Tetrahedron* **1961**, *12*, 186-189.
(2) Willcott, M. R.; Goerland, E. *Tetrahedron Lett.* **1966**, 6341-6345.
(3) Srinivasan, R. *J. Am. Chem. Soc.* **1962**, *84*, 3432-3436, 4141-4145; **1972**, *94*, 8117-8124.
(4) Sustmann, R.; Brandes, D. *Tetrahedron Lett.* **1976**, 1791-1794.
(5) Bloomquist, A. T.; Kwiatek, J. *J. Am. Chem. Soc.* **1951**, *73*, 2098-2100.
(6) Stevens, H. C.; Reich, D. A.; Brandt, D. R.; Fountain, K. R.; Gaughan, E. J. *J. Am. Chem. Soc.* **1965**, *87*, 5257-5259.
(7) Ghosez, L.; Montaigne, R.; Mollet, P. *Tetrahedron Lett.* **1966**, 135-139.
(8) Grieco, P. A. *J. Org. Chem.* **1972**, *37*, 2363-2364.
(9) Vogel, E. *Angew. Chem.* **1956**, *68*, 189.
(10) Dryden, H. L. *J. Am. Chem. Soc.* **1954**, *76*, 2841. Dryden, H. L., Jr.; Burgert, B. E. *J. Am. Chem. Soc.* **1955**, *77*, 5633-5637.
(11) Evans, M. V.; Lord, R. C. *J. Am. Chem. Soc.* **1960**, *82*, 1876-1882; **1961**, *83*, 3409-3413.
(12) Nee, M.; Gorham, W. F.; Roberts, J. D. *J. Org. Chem.* **1981**, *46*, 1021-1022.
(13) Compare: Wiberg, K. B.; Pfeiffer, J. *J. Am. Chem. Soc.* **1968**, *90*, 5324-5325. Wiberg, K. B.; Williams, V. Z., Jr.; Friedrich, L. E. *Ibid.* **1968**, *90*, 5338-5339.

0022-3263/87/1952-4772$01.50/0

Scheme I



2%.[14] An alternative approach from **9**, by way of the tosylhydrazone and a Shapiro elimination with methyllithium, affords only 2.3% of the diene.[5] Our own attempts with this reaction resulted in gas chromatographically pure diene **1** in an improved but still unsatisfactory yield, 5.4% from the tosylhydrazone. The monodeuterio dienes **3** and **10** have been reported,[15,16] but the routes employed provided no useful precedents for our particular needs.

The synthetic challenge posed by our labeling objectives and the record of frustration adhering to the conversions **9** → **1**, **2** or **3** have been met by recourse to an elimination reaction involving radical and anionic intermediates, eschewing electron-deficient species prone to undesired rearrangements.

Results and Discussion

Greene and co-workers prepared a bicyclo[3.2.0]hept-6-ene derivative as part of a synthesis of (+)-hirsutic acid C by reacting the corresponding 7,7-dichloro-6-(mesyloxy)bicyclo[3.2.0]heptane with sodium in liquid ammonia.[17] The reaction presumably involves one-electron transfers and anion–radical, radical, and anionic intermediates, species which we anticipated would tolerate without rearrangements an olefin functionality in the five-membered ring. Application of this reaction to the preparation of bicyclo[3.2.0]hepta-2,6-diene does indeed work extremely well; the sequence outlined in Scheme I gives product **1**, isolated and purified by spinning-band distillation, in 64% overall yield.

Further experience with the sodium/liquid ammonia reduction showed that the reaction was nearly quantitative; by patient evaporation of ammonia after the reaction, use of precooled (5 °C) solvents and solutions for extracts and washes during product isolation, and careful concentration of pentane/diene solutions by distillation, loss of the comparatively volatile product was minimized.

The deuteriated analogues **2**, **5**, and **6** were easily secured as well by this sequence, substituting C_5D_6 for cyclopentadiene or substituting $NaBD_4$ for $NaBH_4$, or both.

Proton NMR spectra at 500 MHz for **1**, **2**, **5**, and **6** (Figure 1) give persuasive evidence for the high specificity and extent of deuterium incorporation attained through Scheme I and simple permutations between deuteriated and undeuteriated reactants.

Straightforward repetition of Scheme I with Na/ND_3 would be expected to give 7-deuteriobicyclo[3.2.0]hepta-2,6-diene, but would also be prohibitively expensive. A more practical alternative was sought and found through selective reduction of the dichloro ketone **11**. Mechanistic considerations enable one to predict that a 7-chloro-6-(mesyloxy)bicyclo[3.2.0]hept-2-ene would be just as suitable in the sodium/liquid ammonia reaction as the 7,7-dichloro-6-(mesyloxy) system **13**, and this expectation did prove correct. Scheme II outlines the single example of this selective reduction tactic carried through, a preparation of perdeuteriobicyclo[3.2.0]hepta-2,6-diene (**8**).

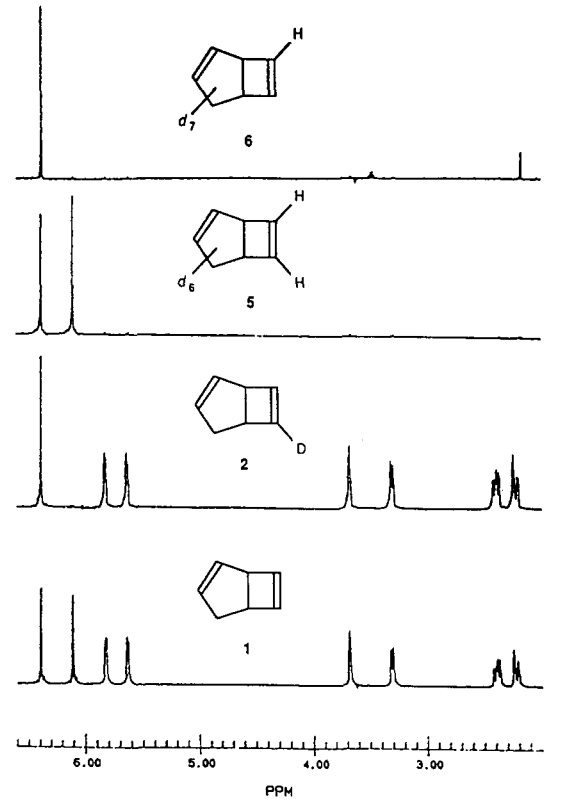
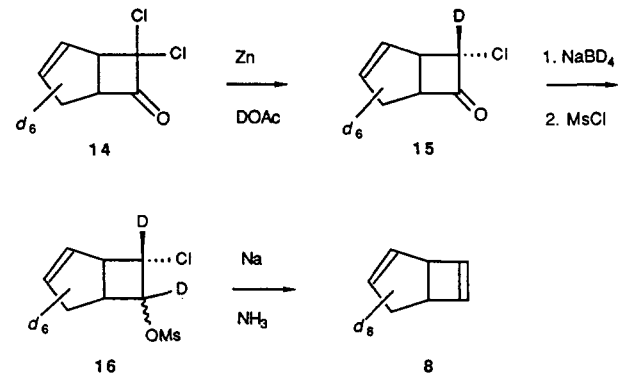


Figure 1. Proton NMR 500-MHz spectra of bicyclo[3.2.0]hepta-2,6-diene (**1**) and deuteriated analogues **2**, **5**, and **6**.

Scheme II



The stereochemical assignments 7-*endo*-chloro in **15** and **16** are based largely on a stereochemical rationale: deuterium donation by DOAc to the 7-chloro enolate anion from the more accessible exo face. The reduction **14** → **15** did appear stereoselective, for when the reaction was followed by capillary GC analysis only one monochloro ketone was detected.

The proton NMR spectrum of **8** showed only very faint absorptions from residual protons at each position; the diene was characterized primarily through capillary GC comparisons with **1** (identical retention times on two columns) and a mass spectrometric confirmation of molecular formula (*m/e* 106, M^+ for C_7D_8).

(14) Baldwin, J. E.; Kaplan, M. S. 1971, unpublished results; *J. Chem. Soc. D* **1970**, 1560–1561; *J. Am. Chem. Soc.* **1971**, *93*, 3969–3977; **1972**, *94*, 668; **1972**, *94*, 4696–4699.
(15) Otterbacher, E. W.; Gajewski, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 5862–5866.
(16) Sustmann, R.; Brandes, D.; Lange, F.; Nüchter, U. *Chem. Ber.* **1985**, *118*, 3500–3512.
(17) Greene, A. E.; Luche, M. J.; Serra, A. A. *J. Org. Chem.* **1985**, *50*, 3957–3962.

Three additional deuteriated bicyclo[3.2.0]hepta-2,6-dienes, **3**, **4**, and **7**, could be synthesized according to Scheme II without difficulty, but have not been prepared.

Thus bicyclo[3.2.0]hepta-2,6-dienes with deuterium labeling as desired, at C1–C5, C6, or C7, are now readily available; the synthetic chemistry developed to secure these compounds should serve as well for certain specifically ^{13}C-labeled bicycloheptadienes.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Triethylamine was distilled from CaH_2, methanesulfonyl chloride was distilled from P_2O_5, and cyclopentadiene was freshly prepared from dicyclopentadiene (Aldrich Chemical Co.) and dried over 4A molecular sieves. All other reagents were used as received from commercial suppliers. Proton NMR spectra were obtained for $CDCl_3$ solutions with Me_4Si at δ 0.0 ppm as internal reference on a General Electric QE-300-MHz spectrometer or GN-500-MHz instrument, interfaced to a VAX 8650 data system. Mass spectral data were secured with Hewlett-Packard (HP) 5890, 5970B, and 9836 instruments and computer. Analytical gas chromatographic (GC) analyses were done with a 0.2-mm i.d. 25-m cross-linked 5% phenyl methyl silicone fused silica capillary column (column A), a 0.2-mm i.d. 25-m cross-linked methyl silicone capillary column (column B), a HP 5780 instrument with FID detectors, and HP 3390A and 3392A reporting integrators (column He flow 1 mL/min, detector temperature 300 °C, injector temperature 160 °C). Preparative GC separations were accomplished with a 0.6 × 300 cm, 20% β,β'-oxydipropionitrile on Chromosorb P column at 40 °C and a Varian Aerograph A90-P3 instrument, with He as the carrier gas.

7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one (11) was prepared from 50 g of cyclopentadiene, 55.7 g of dichloroacetyl chloride, and 39.8 g of triethylamine in hexane.[6-8] The redistilled product (34.7 g) had the following characteristics: bp 51–55 °C (2 mm) [lit.[8] bp 49–50 °C (0.3 mm)]; ^1H NMR δ 5.85–6.10 (m, 1 H), 5.60–5.85 (m, 1 H), 3.90–4.40 (m, 2 H), 2.45–2.80 (m, 2 H); mass spectral ions at *m/e* (relative intensity) 176 (M^+, 1.0), 115 (20.2), 113 (69.2), 78 (12.3), 77 (100), 66 (59.5), 51 (32.2), 50 (18.6), 40 (9.8), 39 (26.7); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), dicyclopentadiene retention times were 4.57 and 4.94 min on column B and column A, respectively, and retention times of **11** were 6.42 and 7.25 min on column B and column A, respectively.

7,7-Dichloro-6-hydroxybicyclo[3.2.0]hept-2-ene (12). Ketone **11** (15 g, 85 mmol) and 400 mL of methanol were placed in a 1-L three-necked flask fitted with a mechanical stirrer and solid addition device (fabricated from Tygon tubing, a large vial, two rubber septa, and pinch clamp) and cooled to 0 °C; sodium borohydride (20.2 g, 0.53 mol, Aldrich) was added in small portions over 2 h by using the solid addition device. The reaction mixture was allowed to warm to room temperature and was stirred for 21 h, and then it was recooled to 0 °C and diluted with a cold mixture of 600 mL of 1 N HCl and 200 mL of ether. The layers were separated, and the aqueous phase was extracted three times with ether. The ethereal extract was washed with water, 1 N HCl, water, saturated $NaHCO_3$, water, and brine, and then it was dried over $MgSO_4$ and filtered. Concentration afforded 14.52 g (96% yield) of alcohol **12** as a colorless liquid: ^1H NMR δ 5.50–6.10 (m, 2 H), 4.25–4.65 (m, 1 H), 3.0–4.0 (m, 2 H), 2.30–2.95 (m, 3 H); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), the exo and endo isomers of **12** had retention times of 7.03 (7.89) and 7.24 (8.06) min on column B (column A), respectively, and were in a ratio of 1:8 with the endo isomer predominating.

7,7-Dichloro-6-(methylsulfonyl)bicyclo[3.2.0]hept-2-ene (13). A solution of 44.9 g of **12** (0.22 mol) in 500 mL of CH_2Cl_2 was placed in a 2-L flask and cooled to 0 °C, and then 137.7 mL of triethylamine (0.99 mol) was added. Methanesulfonyl chloride (56.2 mL, 0.73 mol) was placed in an addition funnel and added slowly over 1.5 h. The bath ice was allowed to melt, thus allowing the reaction mixture to slowly warm to room temperature. After being stirred for 7 h, the reaction mixture was again cooled to 0 °C for workup. A mixture of 500 mL of cold water and 500 mL of CH_2Cl_2 was added to the reaction mixture. It was stirred for 30 min, cold 1 N HCl was added to acidify the mixture, and the layers were separated. The aqueous phase was extracted three times with CH_2Cl_2. The organic extract was washed twice with cold water, twice with cold 1 N HCl, cold water, saturated Na_2CO_3, cold water, and brine, and then dried over $MgSO_4$ and filtered. The resulting dark orange solution was concentrated by rotary evaporation, affording 88 g of a dark orange liquid with a purity of 66% (determined by capillary GC analysis) corresponding to approximately 58 g of **13** (100% yield). This crude mesylate was used without further purification in the synthetic transformation that follows: capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), **13** had retention times of 12.51 and 13.70 min on column B and column A, respectively.

Bicyclo[3.2.0]hepta-2,6-diene (1). Ammonia (1.2 L) was condensed at −78 °C in a 2-L three-necked flask fitted with a mechanical stirrer, a dry ice/acetone condenser, and an addition funnel. Sodium (18.18 g, 0.79 mol) was added in small pieces, producing a deep blue color as cooling was maintained at −78 °C. A solution of 12.1 g of crude dichloro mesylate **13** (0.05 mol) in 225 mL of dry tetrahydrofuran was placed in the addition funnel and added to the Na/NH_3 over 30 min, and then the reaction mixture was allowed to warm to −40 to −35 °C and stirred for 3.5 h. To destroy the excess sodium, NH_4Cl was added until the blue color was gone. The dry ice/acetone condenser and the addition funnel were replaced with two cold water condensers with attached oil bubblers. The reaction mixture was slowly allowed to warm to 0 °C, allowing the NH_3 to evaporate. Water (1 L) was added to dissolve the remaining salts, and then 300 mL of pentane was added. The layers were separated, and the aqueous phase was extracted three times with pentane. The pentane extract was washed with water, 1 N HCl, water, saturated $NaHCO_3$, water, and brine, and then it was dried over $MgSO_4$ and filtered. Concentration, first by distillation with a 85-cm glass helix packed column and then with a 60-cm Teflon spinning-band column, gave 7.15 g of diene **1** in pentane. Distillation with a B and R Instruments micro-spinning-band apparatus afforded 2.93 g (67% yield) of **1**: bp 90–91 °C; ^1H NMR δ 6.39 (d, 1 H), 6.10 (d, 1 H), 5.81 (m, 1 H), 5.63 (m, 1 H), 3.67 (brs, 1 H), 3.29–3.32 (m, 1 H), 2.36–2.43 (m, 1 H), 2.20–2.24 (m, 1 H) (Figure 1); GC/MS analysis, *m/e* (relative intensity) 93 (1.7), 92 (M^+, 26.5), 91 (100), 66 (21.0), 65 (20.9), 63 (8.7), 62 (4.6), 51 (7.3), 50 (5.7), 40 (6.6), 39 (25.4); capillary GC analysis (temperature 45 °C), the retention times of **1** were 3.88 and 4.25 min on column B and column A, respectively.

7,7-Dichloro-6-hydroxybicyclo[3.2.0]hept-2-ene-*6-d*. In a 1-L three-necked flask fitted with a mechanical stirrer and a solid addition device were placed 40 g of **11** (0.23 mol) and 500 mL of methanol. This solution was cooled to 0 °C; sodium borodeuteride (14.31 g, 341.8 mmol, Cambridge Isotope Labs 99 atom % D) was added in small portions over 2 h with the solid addition device. The reaction mixture was allowed to warm to room temperature and stirred for 15 h before being recooled to 0 °C for workup. A cold mixture of 1 N HCl and ether was added. The layers were separated, and the aqueous phase was extracted three times with ether. The ethereal extract was washed with water, 1 N HCl, water, saturated $NaHCO_3$, water, and brine, and then it was dried over $MgSO_4$ and filtered. Concentration afforded 38.64 g (95% yield) of exo and endo alcohols as a colorless liquid: ^1H NMR δ 5.60–6.20 (m, 2 H), 3.8–4.0 (m, 1 H), 3.3–3.6 (m, 1 H), 2.30–2.90 (m, 3 H); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), the exo and endo alcohols had retention times of 7.14 (7.93) and 7.36 (8.15) min on column B (column A), respectively, and were in a ratio of 1:7.6 with the endo isomer predominating.

7,7-Dichloro-6-[(methylsulfonyl)oxy]bicyclo[3.2.0]hept-2-ene-*6-d*. A solution of 35 g of the *d* alcohol prepared immediately above (0.2 mol) in 500 mL of CH_2Cl_2 was placed in a 2-L flask and cooled to 0 °C. Next, 120.4 mL of triethylamine (0.86 mol) was added; methanesulfonyl chloride (49.2 mL, 0.64 mol) was placed in an addition funnel and added slowly over 2 h. The reaction mixture was allowed to warm to room temperature, stirred for 7 h, then cooled again to 0 °C. A mixture of 500 mL of cold water and 500 mL of CH_2Cl_2 was added to the reaction mixture, the two-phase mixture was stirred for 30 min, and then 150 mL of cold 1 N HCl was added to acidify the mixture. The layers were separated, the aqueous phase was extracted three times with

CH_2Cl_2, and the organic extract was washed with cold water, three times with cold 1 N HCl, twice with cold water, saturated Na_2CO_3, cold water, and brine, and then it was dried over $MgSO_4$ and filtered. The resulting dark orange solution was concentrated in vacuo, affording 55 g of a dark orange liquid with a purity of 86.9% (determined by capillary GC analysis) corresponding to approximately 47.8 g of product mesylate (95% yield). This was used without further purification in the synthetic transformation that follows. Capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C) showed product with retention times of 12.40 and 13.61 min on column B and column A, respectively.

Bicyclo[3.2.0]hepta-2,6-diene-*6-d* (2). Ammonia (2.5 L) was condensed at −78 °C in a 5-L three-necked flask fitted with a mechanical stirrer, a dry ice/acetone condenser, and an addition funnel. While cooling was maintained at −78 °C, sodium (64 g, 2.79 mol) was added in small pieces to the ammonia, producing a deep blue color. A solution of 47.8 g of the mesylate-*d* prepared above in 500 mL of dry tetrahydrofuran was placed in the addition funnel and added to the Na/NH_3 over 1 h, and then the reaction mixture was allowed to warm to −40 to −35 °C and stirred for 6 h. To destroy the excess sodium, 150 g of NH_4Cl was added, resulting in disappearance of the blue color. The dry ice/acetone condenser and the addition funnel were replaced with two cold water condensers with attached oil bubblers. The reaction mixture was slowly allowed to warm to 0 °C, allowing the NH_3 to evaporate. Water (1 L) was added to dissolve the remaining salts, and then 300 mL of pentane was added. The layers were separated, and the aqueous phase was extracted three times with pentane. The pentane extract was washed with water, 1 N HCl, water, saturated $NaHCO_3$, water, and brine, and then it was dried over $MgSO_4$ and filtered. Concentration afforded 180 g of a 9.5% solution of **2** (by capillary GC analysis), corresponding to 17.1 g (98.9% yield) of product. Isolation and purification was done by preparative GC: ^1H NMR (ppm in $CDCl_3$) 6.39 (s, 1 H), 5.81 (m, 1 H), 5.63 (m, 1 H), 3.67 (brs, 1 H), 3.29–3.32 (m, 1 H), 2.36–2.43 (m, 1 H), 2.20–2.24 (m, 1 H); GC/MS analysis, *m/e* (relative intensity) 94 (3.2), 93 (M^+, 47.6), 92 (100), 67 (7.8), 66 (51.6), 65 (19.5), 63 (11.5), 51 (10.7), 40 (22.2), 39 (34.6), 38 (11.7); capillary GC analysis (temperature 45 °C), retention times of **2** were 3.73 and 4.11 min on column B and column A, respectively.

Cyclopentadiene-d_6. A solution of 5 N NaOD (13 mL, prepared by careful addition of sodium to D_2O at 0 °C) was transferred to a 300-mL three-necked flask fitted with a mechanical stirrer, two rubber septa, and a stopcock at the bottom, containing 16.53 g of cyclopentadiene (250 mmol), 5.6 mL of benzene (as an internal NMR standard, to facilitate monitoring the extent of deuteriation of the cyclopentadiene), 2.85 g of benzyltriethylammonium chloride (12.5 mmol), and 150 mL of hexane. The two-phase mixture was stirred vigorously at room temperature until no further change in percent cyclopentadiene exchanged was observed by ^1H NMR. The aqueous layer was then removed via the stopcock in the bottom of the flask. Additional 5 N NaOD (15 mL) and 2.85 g of the phase-transfer catalyst were added for the second exchange, and this process was repeated for a total of eight exchanges. The percent deuterium exchange, as determined by ^1H NMR spectral analysis, and reaction times for the eight exchanges were: first (6 h, 56%), second (6.5 h, 72%), third (15.5 h, 82%) fourth (19.5 h, 91%), fifth (10 h, 94%), sixth (10.5 h, 96%), seventh (22.5 h, 97%), eighth (22 h, >98%). After the final exchange, a thick brown emulsion remained. This was passed through a Celite packed column under a nitrogen atmosphere, and the filtrate was collected in a flask cooled to −78 °C. A brown solid formed along with a yellow liquid. The liquid was decanted and found (by capillary GC analysis) to contain both cyclopentadiene-d_6 and deuteriated dicyclopentadiene. Simple distillation gave a solution of benzene, hexane, and product, estimated by weight and GC analysis to contain 8.8 g of cyclopentadiene-d_6 (49% yield), which was used without further purification. Analysis of the pot residue by GC revealed 6.8 g (38%) of deuteriated dicyclopentadiene.

7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one-*1,2,3,4,4,5-*d_6 (14) was prepared from 8.8 g of cyclopentadiene-d_6, 7.82 mL of dichloroacetyl chloride, and 12 mL of triethylamine in 275 mL of hexane, following established procedures.[6-8] The ketone **14** obtained [10.5 g, 71% yield, bp 65 °C (2 mm)] had the following: mass spectral analysis, *m/e* (relative intensity) 182 (M^+, 1.1), 147 (1.7), 119 (63.8), 82 (100), 72 (57.1), 71 (7.4), 70 (7.4), 54 (31.7), 52 (18.6), 42 (30.8), 40 (14.1); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), the retention times of **14** were 6.15 and 7.22 min on columns B and A, respectively.

7,7-Dichloro-6-hydroxybicyclo[3.2.0]hept-2-ene-*1,2,3,4,4,5-*d_6 was prepared following the procedure given for the undeuteriated system **12** with 7.28 g of **14** (40 mmol), 9.46 g of sodium borohydride (250 mmol), and 500 mL of methanol. The product (7.4 g, 100% yield) was obtained as a colorless liquid: GC/MS analysis, *m/e* (relative intensity); 149 (0.5), 148 (0.9), 105 (14.6), 85 (10.0), 84 (8.4), 82 (12.2), 81 (11.8), 73 (9.9), 72 (100), 71 (14.7), 70 (7.0), 54 (11.5), 42 (20.6); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), the exo and endo alcohols had retention times of 6.78 (7.80) and 7.00 (8.02) min on column B (column A), and were formed in a ratio of 1:8, respectively.

7,7-Dichloro-6-[(methylsulfonyl)oxy]bicyclo[3.2.0]hept-2-ene-*1,2,3,4,4,5-*d_6 was prepared from 7.4 g (40.2 mmol) of the d_6 alcohol described immediately above, 24.7 mL of triethylamine (177 mmol), 10.1 mL of methanesulfonyl chloride (130 mmol), and 250 mL of CH_2Cl_2. The crude mesylate (12.2 g) was obtained as a dark orange oil estimated to be 84% pure by capillary GC analysis, corresponding to a 97% yield: GC/MS analysis, *m/e* (relative intensity) 192 (0.2), 183 (0.9), 130 (8.3), 118 (6.5), 82 (15.4), 81 (11.7), 79 (9.2), 73 (5.4), 72 (100), 71 (16.8), 70 (5.4), 54 (7.4), 42 (9.9); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), the retention times of the mesylates were 12.17 and 13.66 min on columns B and A, respectively.

Bicyclo[3.2.0]hepta-2,6-diene-*1,2,3,4,4,5-*d_6 (5) from the reaction of 10.3 g of mesylate-d_6 with $NaNH_2$, derived from 17.9 of sodium and 1 L of liquid ammonia in 200 mL of THF, was obtained in 62% yield: preparative GC of the purified diene showed ^1H NMR absorptions at 6.39 (d, 1 H) and 6.10 (d, 1 H) as shown in Figure 1; GC/MS analysis, *m/e* (relative intensity) 99 (3.1), 98 (M^+, 42.1), 97 (58.2), 96 (100), 72 (32.4), 70 (13.2), 69 (15.3), 68 (10.6), 42 (29.3), 41 (19.3), 40 (15.2); capillary GC analysis (45 °C) the retention times of **5** were 3.49 and 4.14 min on columns B and A, respectively.

7,7-Dichloro-6-hydroxybicyclo[3.2.0]hept-2-ene-*1,2,3,4,4,5,6-*d_7 was prepared by the method presented for the preparation of **12** from 364 mg (2.0 mmol) of 14, 446 mg of sodium borodeuteride (10.7 mmol, Sigma Chemical Co., 98 atom % D), and 5 mL of methanol-*d* (Aldrich, 99.5+ % D). For the d_7 alcohol (343 mg, 92.2% yield): GC/MS analysis, *m/e* (relative intensity) 166 (0.1), 164 (0.1), 119 (6.9), 105 (17.5), 86 (7.8), 85 (11.0), 82 (18.7), 81 (9.2), 73 (9.2), 72 (100), 71 (9.2), 70 (7.3), 54 (11.9), 52 (7.1), 44 (7.7), 42 (19.6); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), the exo and endo alcohols had retention times of 6.70 (7.74) and 6.90 (7.94) min on column B (column A) and were formed in a ratio of 1:9, respectively.

7,7-Dichloro-6-[(methylsulfonyl)oxy]bicyclo[3.2.0]hept-2-ene-*1,2,3,4,4,5,6-*d_7 was prepared by the method given above for the unlabeled analogue **13**, from 343 mg (1.84 mmol) of d_7 alcohol, 818 mg of triethylamine (8.08 mmol), 681 mg of methanesulfonyl chloride (5.94 mmol), and 5 mL of CH_2Cl_2. The crude mesylate product obtained (492 mg) was of 86.2% purity by capillary GC analysis, corresponding to an 88% yield: GC/MS analysis, *m/e* (relative intensity) 191 (0.1), 186 (0.3), 131 (7.2), 119 (7.3), 82 (21.2), 79 (9.0), 73 (5.4), 72 (100), 71 (12.8), 70 (6.3), 54 (9.2), 42 (13.3); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), the retention times of the mesylate-d_7 were 12.04 and 13.55 min on columns B and A, respectively.

Bicyclo[3.2.0]hepta-2,6-diene-*1,2,3,4,4,5,6-*d_7 (6) was prepared by the method presented for the preparation of **1** with 50 mL of liquid NH_3, 740 mg of sodium (32.2 mmol), 424 mg of mesylate-d_7 (1.61 mmol), and 10 mL of THF. Crude diene **6** (574 mg) was obtained (29% purity by capillary GC analysis) corresponding to a quantitative conversion from mesylate to **6**: ^1H NMR δ 6.39 (s, 1 H); GC/MS analysis, *m/e* (relative intensity) 100 (2.8), 99 (M^+, 34.5), 98 (32.8), 97 (100), 96 (13.0), 72 (28.7), 71 (8.0), 70 (14.0), 69 (14.2), 54 (7.0), 52 (6.8), 44 (9.6), 42 (30.5); capillary GC analysis (45 °C), retention times of **6** were 3.47 and 4.11 min on columns B and A, respectively.

7-Chlorobicyclo[3.2.0]hept-2-en-6-one-*1,2,3,4,4,5,7-*d_7 (15). Ketone **14** (364 mg, 2.0 mmol) was dissolved in 1 mL of acetic acid-*d* (Norell, 99 atom % D) and added to 131 mg of zinc dust

(2.0 mmol). The suspension was stirred at room temperature with periodic monitoring by capillary GC. After 3 h, the relative amounts of product and starting material remained constant, so 32 mg of zinc (0.5 mmol) was added. After 30 min, the starting material was consumed. The reaction mixture was filtered, and the solid was washed with several small portions of ether. The filtrate was washed with 1 N $NaHCO_3$, water, and brine, and then it was dried over $MgSO_4$ and filtered. Concentration provided 223 mg of **15** (75.2% yield) as a pale yellow liquid: GC/MS analysis, *m/e* (relative intensity) 149 (M^+, 0.3), 114 (2.2), 86 (100), 85 (74.3), 82 (41.9), 81 (18.3), 72 (67.9), 71 (9.5), 70 (10.0), 54 (22.1), 42 (43.6); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), the retention times of **15** were 5.71 and 6.88 min on columns B and A, respectively.

7-Chloro-6-[(methylsulfonyl)oxy]bicyclo[3.2.0]hept-2-ene-*1,2,3,4,4,5,6,7-d*$_8$ (16) was prepared from the d_7 ketone (215 mg), using 380 mg of sodium borodeuteride (9.08 mmol, Sigma, 98 atom % D), 3 mL of methanol-*d* (Aldrich, 99.5+ atom % D) for the reduction (64% yield), and 340 mg of methanesulfonyl chloride for the mesylation (99% yield): GS/MS analysis, *m/e* (relative intensity) 195 (0.1), 98 (15.0), 86 (20.5), 85 (4.4), 82 (15.9), 81 (4.2), 73 (5.1), 72 (100), 71 (11.9), 70 (8.0), 54 (7.9), 42 (18.6); capillary GC analysis (temperature increase 10 °C/min from 80 to 250 °C), the retention times of **16** were 11.72 and 13.34 min on columns B and A, respectively.

Bicyclo[3.2.0]hepta-2,6-diene-*1,2,3,4,4,5,6,7-d*$_8$ (8) was prepared by the method presented for the preparation of 1 with 50 mL of liquid NH_3, 420 mg of sodium (18.2 mmol), 210 mg of mesylate-d_8 (0.91 mmol), 3 mL of pentane, 6 mL of THF, and 8 mL of ether. A concentrated solution of 8 was obtained. Isolation and purification was accomplished by preparative GC: GC/MS analysis, *m/e* (relative intensity) 101 (2.3), 100 (M^+, 29.3), 99 (13.7), 98 (100), 97 (19.9), 73 (2.2), 72 (29.6), 71 (5.5), 70 (24.1), 54 (10.2), 42 (39.5), 40 (19.5); capillary GC analysis (45 °C), the retention times of 8 were 3.49 and 4.14 min on columns B and A, respectively.

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged.

Registry No. 1, 2422-86-8; **2**, 110097-50-2; **5**, 110097-51-3; **6**, 110097-52-4; **8**, 110097-53-5; **11**, 5307-99-3; **12** (isomer 1), 19296-96-9; **12** (isomer 2), 19296-95-8; **12-6-*d*** (isomer 1), 110097-55-7; **12-6-*d*** (isomer 2), 110171-08-9; **12-*1,2,3,4,4,5*-d_6** (isomer 1), 110097-61-5; **12-*1,2,3,4,4,5*-d_6** (isomer 2), 110171-09-0; **12**, *1,2,3,4,4,5,6*-d_7 (isomer 1), 110097-63-7; **12-*1,2,3,4,4,5,6*-d_7** (isomer 2), 110171-11-4; **13** (isomer 1), 110097-54-6; **13** (isomer 2), 110171-07-8; **13-*6*-*d***, 110097-59-1; **13-*1,2,3,4,4,5*-d_6** (isomer 1), 110097-62-6; **13-*1,2,3,4,4,5*-d_6** (isomer 2), 110171-10-3; **13-*1,2,3,4,4,5,6*,-d_7** (isomer 1), 110097-64-8; **13-*1,2,3,4,4,5,6*-d_7** (isomer 2), 110171-12-5; **14**, 110097-56-8; **15**, 110097-57-9; **16** (isomer 1), 110097-58-0; **16** (isomer 2), 110171-13-6; cyclopentadiene, 542-92-7; cyclopentadiene-d_6, 2102-16-1; dicyclopentadiene-d_x, 110097-60-4; dichloroacetyl chloride, 79-36-7.

A Stereochemical Study of the Thermolysis of *cis-anti-* and *trans*-1,2-Dimethyl-*cis*-3,4-dideuteriocyclobutane

Yen-Seine Wang and James S. Chickos*

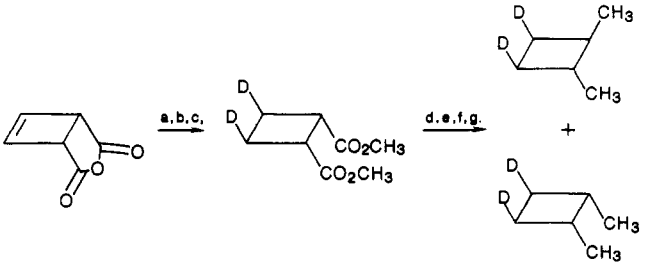
Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121

Received March 30, 1987

The stereochemistry of the fragmentation and isomerization of *cis-anti-* and *trans*-1,2-dimethyl-*cis*-3,4-dideuteriocyclobutane at 510 °C is reported. The cis-anti-cis isomer undergoes fragmentation to yield *cis/trans*-propene-d_1 (1.5/1, major pathway), *cis/trans*-2-butene (1.4/1), and *cis/trans*-ethylene-d_2 (1/1, minor pathway). Recovered *cis*-1,2-dimethylcyclobutane-d_2 contained approximately 40% of the double rotation product relative to the product of single methyl rotation, *trans-1,2-dimethylcyclobutane-*d_2. The trans isomer behaves similarly, yielding *cis/trans*-propene-d_1 (1/1, major pathway), *cis/trans*-2-butene (1/5), and *cis/trans*-ethylene-d_2 (1/1, minor pathway). Recovered *cis*-1,2-dimethylcyclobutane-d_2 from thermolysis of the trans isomer consists mainly of equal amounts of *cis-anti-cis-* and *cis-syn-cis*-1,2-dimethylcyclobutane-d_2 as analyzed by NMR. On the basis of product composition, the thermal chemistry of this system can be explained as proceeding through 2,5-hexanediyl (major pathway) and 3-methyl-1,4-pentanediyl (minor pathway). On the basis of the observed stereochemistry, it can be concluded that the lifetimes of both 2,5-hexanediyl and 3-methyl-1,4-pentanediyl are similar and of the same order as bond rotations at a radical center. This suggests that the gauche to trans conformational changes involving carbon–carbon bond rotation at carbons 2 and 3 of 1,4-diyls may not be competitive with fragmentation.

The thermolysis of *cis-* and *trans*-1,2-dimethylcyclobutane by Gerberich and Walters[1] is a classic kinetic study of cyclobutane decomposition. Since then, several different aspects of the thermal behavior of this chemical system have been reported. Scrinivasan and Hsu[2] have investigated the stereochemistry of recovered ethylene-d_2 from the thermolysis of *cis*-1,2-dimethyl-*anti-cis*-3,4-dideuteriocyclobutane and found extensive scrambling of stereochemistry. More recently, Dervan et al.[3] have investigated the thermal behavior of *cis-* and *trans*-3,4- and *cis-* and *trans*-3,6-dimethyl-3,4,5,6-tetrahydropyridazines and found similar product distributions from both 1,2-dimethylcyclobutane and 3,4- and 3,6-dimethyltetrahydropyridazine thermolyses. Starting off with different precursors, their analysis demonstrated that access to the

Scheme I. Synthesis of *cis-anti-* and *trans*-1,2-Dimethyl-*cis*-3,4-dideuteriocyclobutane[a]



[a] (a) D_2–Pd/C; (b) H_2O; (c) CH_2N_2; (d) CH_3ONa/CH_3OH; (e) LAH; (f) TsCl/pyridine; (g) LAH.

(1) Gerberich, H. R.; Walters, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 3935, 4884.
(2) Scrinivasan, R.; Hsu, J. N. C. *J. Chem. Soc., Chem Commun.* **1972**, 1213.
(3) Dervan, P. B.; Uyehara, T.; Santilli, D. S. *J. Am. Chem. Soc.* **1979**, *101*, 2069.

0022-3263/87/1952-4776$01.50/0