

# Electronic Structure of Symmetric Homoconjugated Dienes. Circular Dichroism of (1*S*)-2-Deuterio- and 2-Methylnorbornadiene and (1*S*)-2-Deuterio- and 2-Methylbicyclo[2.2.2]octadiene

David A. Lightner,<sup>\*1a</sup> Jacek K. Gawroński,<sup>1a,b</sup> and Thomas D. Bouman<sup>1c</sup>

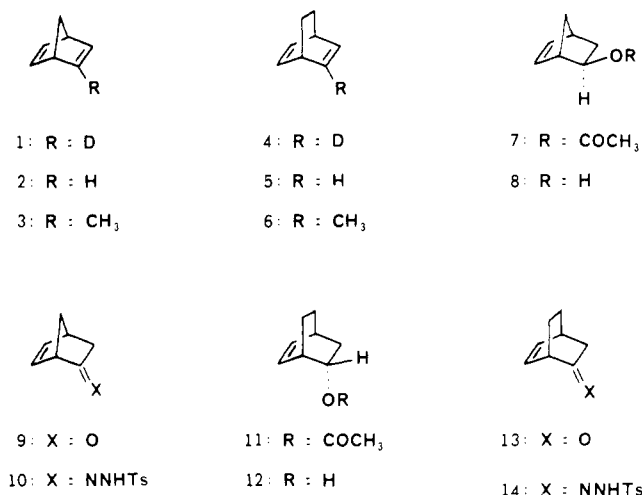
Contribution from the Departments of Chemistry, University of Nevada, Reno, Nevada 89557, and Southern Illinois University, Edwardsville, Illinois 62026. Received March 6, 1980

**Abstract:** (1*S*)-[2-<sup>2</sup>H]Bicyclo[2.2.1]hepta-2,5-diene (**1**), (1*S*)-2-methylbicyclo[2.2.1]hepta-2,5-diene (**3**), (1*S*)-[2-<sup>2</sup>H]bicyclo[2.2.2]octa-2,5-diene (**4**), and (1*S*)-2-methylbicyclo[2.2.2]octadiene (**6**) were prepared by reaction of the corresponding chiral  $\beta,\gamma$ -unsaturated ketone tosylhydrazone with  $\text{CH}_3\text{Li}$  followed by either  $\text{D}_2\text{O}$  or  $\text{CH}_3\text{I}$  quenching. The circular dichroism Cotton effects of **1** ( $\Delta\epsilon_{237} = -0.032$ ,  $\Delta\epsilon_{216} = +0.14$ ,  $\Delta\epsilon_{205} = -0.37$ ) and **4** ( $\Delta\epsilon_{222} = -0.027$ ) are the first examples obtained from deuterated olefins or dienes whose chirality is due only to isotopic substitution. Both the deuterated and the methylated dienes exhibited multiple Cotton effects (**3**,  $\Delta\epsilon_{249} = +2.38$ ,  $\Delta\epsilon_{222} = -0.25$ ,  $\Delta\epsilon_{219} = -0.54$ ,  $\Delta\epsilon_{214} = +0.62$ ,  $\Delta\epsilon_{204} = -0.94$ ; **6**,  $\Delta\epsilon_{231} = +0.90$ ,  $\Delta\epsilon_{211} = +0.48$ ,  $\Delta\epsilon_{200} = -0.24$ ), demonstrating the existence of interchromophoric interaction and electronic transitions that are only difficultly seen in their ultraviolet spectra. We present ab initio localized orbital RPA calculations on **1** that allow a consistent assignment of norbornadiene transitions.

## Introduction

Although there has been considerable recent interest and success in observing circular dichroism (CD) Cotton effects (CEs) for the electric dipole forbidden  $n \rightarrow \pi^*$  transitions of chiral deuterio ketones,<sup>2,3</sup> where deuterium is the isolated perturber, there have been no examples reported of CD CEs for deuterium perturbors on carbon-carbon double bonds, except in the aromatic chromophore of [2.2]paracyclophane.<sup>4</sup> This is not surprising, because chiral isotopic perturbations are generally weak,<sup>2</sup> and it thus becomes correspondingly difficult to measure CEs for electronic transitions that are strongly electric dipole allowed. However, in judiciously chosen structures containing symmetric homoconjugated diene chromophores we were able to measure CD spectra. We chose bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) and bicyclo[2.2.2]octa-2,5-diene as suitable models because both are fairly rigid structures with chromophores of theoretical interest.<sup>5-15</sup>

Chart I



The structural rigidity is useful in reducing the effects of conformational variables when assessing the influence of deuterium perturbation.<sup>2a</sup> The parent molecules are also achiral; hence, they provide the greatest opportunity for isolating and observing the influence of deuterium perturbation. They also offered the opportunity to observe electronic transitions (through interaction of the two ethylenic units) in their CD spectra that are otherwise difficult to detect in their ordinary absorption spectra. We therefore describe in this work the syntheses and CD spectra of (1*S*)-2-deuteriobicyclo[2.2.1]hepta-2,5-diene (**1**) and (1*S*)-2-deuteriobicyclo[2.2.2]octa-2,5-diene (**4**) and their corresponding methyl (in place of deuterium) derivatives **3** and **6** (Chart I), and we present an ab initio theoretical treatment of the UV and CD spectra of **1**.

- (1) (a) University of Nevada. (b) On leave from Adam Mickiewicz University, Poznan, Poland. (c) Southern Illinois University, Edwardsville.  
 (2) (a) Lightner, D. A.; Gawroński, J. K.; Bouman, T. D. *J. Am. Chem. Soc.*, **1980**, *102*, 1983-1990. (b) Simek, J. W.; Mattern, D. L.; Djerassi, C. *Tetrahedron Lett.* **1975**, 3671-3674. (c) Lightner, D. A.; Chang, T. C.; Horwitz, J. *Ibid.* **1977**, 3019-3020. Errata: *Ibid.* **1978**, 696. (d) Djerassi, C.; VanAntwerp, C. L.; Sundararaman, P. *Ibid.* **1978**, 535-538. (e) Meyer, W. L.; Lobo, A. P.; Ernstbrunner, E. E.; Giddings, M. R.; Hudec, J. *Ibid.* **1978**, 1771-1774. (f) Numan, H.; Wynberg, H. *J. Org. Chem.* **1978**, *43*, 2232-2236. (g) Lee, S. F.; Barth, G.; Kieslich, K.; Djerassi, C. *J. Am. Chem. Soc.* **1978**, *100*, 3965-3966. (h) Sundararaman, P.; Djerassi, C. *Tetrahedron Lett.* **1978**, 2457-2460. Errata: *Ibid.* **1979**, 4120. (i) Pak, C. S.; Djerassi, C. *Ibid.* **1978**, 4377-4378. (j) Levine, S. G.; Gopalakrishnan, B. *Ibid.* **1979**, 699-702. (k) Burgstahler, A. W.; Sanders, M. E. *Ibid.* **1979**, 2509-2510. (l) Sing, Y. L.; Numan, H.; Wynberg, H.; Djerassi, C. *J. Am. Chem. Soc.* **1979**, *101*, 5155-5158. Errata: *Ibid.* **1979**, *101*, 7439. (m) Konopelski, J. P.; Sundararaman, P.; Barth, G.; Djerassi, C. *Ibid.*, **1980**, *102*, 2737-2745.  
 (3) For early work, see: (a) Djerassi, C.; Closson, W.; Lippman, A. E. *J. Am. Chem. Soc.* **1956**, *78*, 3163-3166. (b) Djerassi, C.; Tursch, B. *Ibid.* **1961**, *83*, 4609-4612. (c) Meyer, W. L.; Lobo, A. P. *Ibid.* **1966**, *88*, 3181-3182. (d) Kokke, W. C. M. C.; Oosterhoff, L. J. *Ibid.* **1972**, *94*, 7583-7584. (e) Kokke, W. C. M. C.; Varkevissier, F. A. *J. Org. Chem.* **1974**, *39*, 1653-1656.  
 (4) Hoffman, P. H.; Ong, E. C.; Weigang, Jr., O. E.; Nugent, M. J. *J. Am. Chem. Soc.* **1974**, *96*, 2620-2621. Hasslock, M. A.; Nugent, M. J.; Weigang, Jr., O. E. *Ibid.* **1974**, *96*, 2619-2620.  
 (5) Wilcox, C. F.; Winstein, S.; McMillan, W. G. *J. Am. Chem. Soc.* **1960**, *82*, 5450-5454.  
 (6) Hermann, R. B. *J. Org. Chem.* **1962**, *27*, 441-442.  
 (7) Robin, M. B.; Kuebler, N. A. *J. Chem. Phys.* **1966**, *44*, 2664-2671.  
 (8) Robin, M. B.; Kuebler, N. A. *J. Mol. Spectrosc.* **1970**, *33*, 274-291.  
 (9) Yamakawa, M.; Kubota, T. *Shionogi Kenkyusho Nempo* **1965**, *15*, 109-124; *Chem. Abstr.* **1966**, *64*, 12053b.  
 (10) Wilcox, C. F.; Whitney, G. C. *J. Org. Chem.* **1967**, *32*, 3348-3351.

- (11) Hoffmann, R.; Heilbronner, E.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 706-707.  
 (12) Palmer, M. H.; Findley, R. H. *Chem. Phys. Lett.* **1972**, *15*, 416-420.  
 (13) de Meijere, A.; Meyer, L.-U. *Tetrahedron Lett.* **1974**, 2051-2054.  
 (14) (a) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936-967. (b) Frueholz, R. P.; Flicker, W. M.; Mosher, O. A.; Kuppermann, A. *J. Chem. Phys.* **1979**, *70*, 1986-1993.  
 (15) Lauer, G.; Schulte, K. W.; Schweig, A. *J. Am. Chem. Soc.* **1978**, *100*, 4925-4935.

### Synthesis and Stereochemistry

We believed and expected that the chiral dienes might be synthesized by judicious quenching in the base-catalyzed tosylhydrazone elimination reactions<sup>16,17</sup> of **10** and **14**. For the preparation of optically active dienes **1** and **3**, the key intermediate was (–)-norbornenyl acetate (**7**)<sup>18</sup> obtained via asymmetric hydroboration of norbornadiene (**2**).<sup>19</sup> Hydrolysis of **7** to its alcohol (**8**) was achieved by use of LiAlH<sub>4</sub>. Oxidation of **8** was accomplished with pyridinium chlorochromate<sup>20</sup> to give **9** in 24% yield. Oxidation of **8** to **9** has been achieved in similarly low yields with a variety of reagents: aluminum *tert*-butoxide–quinone in benzene (16%),<sup>19</sup> active MnO<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (57%),<sup>21</sup> and Jones oxidation (≤36%).<sup>22</sup> We recommend the less acidic pyridinium dichromate,<sup>23</sup> which we used in the oxidation of **12** to **13**. Ketone **9** was converted to **10** by reaction with *p*-toluenesulfonylhydrazine, and **10** was converted either to **1** or **3** first by reaction with CH<sub>3</sub>Li in tetramethylethylenediamine (TMEDA)<sup>16</sup> at low temperature, then quenching with D<sub>2</sub>O<sup>16b,c</sup> to give **1** or CH<sub>3</sub>I<sup>16d</sup> to give **3**. By use of TMEDA as solvent we could minimize CH<sub>3</sub>Li addition to the C=N bond of the tosylhydrazone and also obtain nearly 100% deuterium incorporation in a 67% (isolated by GC) yield.

The absolute configurations of **7**–**9** had been determined previously by the chemical conversion of the enantiomers of **8** or **9** to (+)-norcamphor.<sup>19</sup> The absolute configuration of (–)-norcamphor was determined earlier by its conversion to (–)-fenchone.<sup>24</sup> The assignment of absolute configuration of **8** was confirmed by LIS-NMR (lanthanide-induced shift–nuclear magnetic resonance) measurements<sup>25</sup> of its (*R*)-(+)– $\alpha$ -methoxy- $\alpha$ -trifluoromethylphenylacetate ester (Mosher ester).<sup>26</sup> The enantiomeric excess (ee) of **8** was determined to be 48% by <sup>19</sup>F NMR measurements of its Mosher ester<sup>25,27</sup> and the ee of **9** by comparison of its large  $[\alpha]_D$  with previously reported values.<sup>28,29</sup> We carefully and successfully avoided enantiomeric fractionation in the conversion of **9** to **10** and in the isolation of **10**. This was demonstrated in the conversion of **10** back to **9** with an  $[\alpha]_D$  identical with that of starting ketone **9**. Therefore we conclude that **1** and **3** are obtained in 48% ee.

Similarly, (1*S*)-endo-2-acetoxycyclo[2.2.2]oct-5-ene (**11**)<sup>19,30,31</sup>

(16) (a) Shapiro, R. H. *Org. React.* **1976**, *23*, 405–407. (b) Stemke, J. E.; Bond, F. T. *Tetrahedron Lett.* **1975**, 1815–1818. (c) Shapiro, R. H.; Lipton, M. F.; Kolonko, K. J.; Bushwell, R. L.; Capuano, L. A. *Ibid.* **1975**, 1811–1815. (d) Stemke, J. E.; Chamberlin, A. R.; Bond, F. T. *Ibid.* **1976**, 2947–2950.

(17) The reaction is ordinarily achieved with an alkyl lithium as base; however, lithium diisopropylamide/THF has been used recently to prepare 7,7-dimethylnorbornadiene from dehydro- $\alpha$ -fenchocamphorone tosylhydrazone. The reaction gave an unexpected byproduct, 7,7-dimethylbicyclo[2.2.1]hept-2-ene. The authors offer no explanation. It seems probable that the abnormal product is not due to the Shapiro–Heath reaction but rather to an artifact (7,7-dimethylbicyclo[2.2.1]heptan-2-one tosylhydrazone) produced during the prolonged reflux of *p*-toluenesulfonylhydrazine with dehydro- $\alpha$ -fenchocamphorone. Jefford, C. W.; Wallace, T. W.; Huang Can, N.-T.; Rimbault, C. G. *J. Org. Chem.* **1979**, *44*, 689–691.

(18) We thank Dr. C. S. Pak of this laboratory for a sample of this material.

(19) Mislow, K.; Berger, J. G. *J. Am. Chem. Soc.* **1962**, *84*, 1956–1961.

(20) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647–2650.

(21) On a mixture of 21% *exo* and 79% *endo* alcohols, ref 19.

(22) Pak, C. S. Ph.D. Dissertation, University of Nevada, Reno, 1977.

(23) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399–402.

(24) Berson, J. A.; Walia, J. S.; Remanick, A.; Suzuki, S.; Reynolds-Warnhoff, P.; Willner, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 3986–3997.

(25) Kalyanam, N.; Lightner, D. A. *Tetrahedron Lett.* **1979**, 415–418.

(26) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543–2549.

(27) Pak, C. S. Ph.D. Dissertation, University of Nevada, Reno, 1977. Dr. Pak determined that **7** of  $[\alpha]_D^{25} -23.97^\circ$  (neat) and its alcohol (**8**) of  $[\alpha]_D^{25} +5.91^\circ$  (c 8.7, CHCl<sub>3</sub>) had a 48% ee as determined by <sup>19</sup>F NMR on the Mosher ester of **8**. This corresponds to an  $[\alpha]_D^{25} -550^\circ$  (c 0.17, isooctane) for **9** of 48% ee.

(28) Sandman, D. J.; Mislow, K. *J. Org. Chem.* **1968**, *33*, 2924–2926. These authors report  $[\alpha]_D^{25} -525^\circ$  (c 0.169, isooctane) for **9** of 45.2% ee based on relative integrated areas of the methoxymethine resonances in the 100-MHz NMR of the corresponding *endo*-norbornenyl *O*-methylmandelate. Reference 19 cites  $[\alpha]_D^{25} +548^\circ$  (c 1.7, CHCl<sub>3</sub>) for enantiomer, 48% ee.

(29) Berson, J. A.; Suzuki, S. *J. Am. Chem. Soc.* **1959**, *81*, 4088–4094. These authors determined the ee of norbornyl half-acid phthalate by isotopic dilution. These data could be related to the ee of **9** by chemical conversion of **9** to norcamphor.

was converted to the alcohol (**12**) with LiAlH<sub>4</sub> and oxidized to the corresponding ketone (**13**) with pyridinium dichromate<sup>23</sup> in 61% isolated yield. Other methods of oxidizing **12** to **13** include aluminum isopropoxide–benzophenone (no reported yield),<sup>19</sup> active MnO<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> (64%),<sup>19,32</sup> and dichromate–ether (40%).<sup>32</sup> We favor the more facile pyridinium dichromate oxidation. Preparation of **4** and **6** via the tosylhydrazone (**14**) of **13** proceeded smoothly, without enantiomeric fractionation and with deuterium incorporation. The Shapiro olefin synthesis<sup>16</sup> is faster with **14** than with **10** and gives higher yields—probably because of diminished strain and steric crowding in the former.

The absolute configuration of **12** has been determined by its conversion to the (+)-dihydro derivative,<sup>19,33</sup> which has been obtained from (–)-*exo*-2-aminomethylnorbornane.<sup>33</sup> The absolute configurational assignment of **12** correlated exactly with LIS-NMR measurements on its Mosher ester.<sup>25</sup> The ee of **12** was determined to be 76% by <sup>19</sup>F NMR of the Mosher ester<sup>25</sup> and by comparison of the  $[\alpha]_D$  of **13** to previously determined values<sup>31,33</sup> which had been correlated with and derived from isotopic dilution studies on the half-acid phthalate ester of **12**.<sup>32</sup> Here, as in the bicyclo[2.2.1]heptane series, we could determine that no enantiomeric fractionation occurred in going from **13** to **4** to **5**, to which we therefore assign a 76% ee.<sup>34</sup>

### Results and Discussion

**Interaction of Chromophores.** Interatomic distances and bond angles, measured by electron diffraction, clearly show the close proximity of the double bonds or norbornadiene (**2**).<sup>35,36</sup> The dihedral angle ( $\theta$ ) between the C=C groups has a value of ca. 115° with a C<sub>2</sub>–C<sub>6</sub> distance of 2.42 Å. These data provide a basis for expecting electronic interaction between the two olefinic chromophores of **2** resulting in UV transitions that are more complex than those exhibited by norbornene, the related monoolefin. Indeed, many studies have been directed toward the detection and theoretical explanation of the electronic interaction of the C=C groups of **2** dating from the work of Wilcox, Winstein, and McMillan.<sup>5</sup> Those authors measured and compared the solution- and vapor-phase UV spectra of **2** and norbornene (Table I) in which they clearly saw the presence of new and different transitions of **2** not found in norbornene. They interpreted the spectra on the basis of Hückel and Pariser–Parr  $\pi$ -electron calculations, which predicted a forbidden long-wavelength transition at 214 nm (Table I), and concluded that the complex series of peaks constituting the 211-nm band is a forbidden <sup>1</sup>A<sub>1</sub> → <sup>1</sup>A<sub>2</sub>  $\pi$ – $\pi^*$  transition. Hermann<sup>6</sup> reached a similar conclusion in his Pariser–Parr  $\pi$ -electron calculations, which predicted an <sup>1</sup>A<sub>1</sub> → <sup>1</sup>A<sub>2</sub> transition at 208 nm and an <sup>1</sup>A<sub>1</sub> → <sup>1</sup>B<sub>2</sub> transition at 188 nm (Table I).

The UV spectrum of **2** was subsequently reinvestigated by Yamakawa and Kubota<sup>9</sup> (Table I) and by Robin and Kuebler.<sup>7,8</sup> The latter authors determined that the “211 nm band” is actually due to (at least) two overlapping transitions: (1) a valence shell excitation with 1200-cm<sup>–1</sup> vibrational spacing, which they assigned to N → V<sub>1</sub>, and (2) a more prominent allowed Rydberg excitation ( $\pi$ – $\sigma^*$ ?) centered at 221 nm and having 385-cm<sup>–1</sup> vibrational spacing. The Rydberg excitation becomes indistinct by He pressure broadening in the gas phase. More recent work on **2** has been devoted to detecting interchromophoric interaction by photoelectron (PE)<sup>14a</sup> and electron impact<sup>14b</sup> spectroscopy and to rationalizing the available UV and PE data by molecular orbital calculations (Table I).<sup>11,14a,15</sup>

(30) We thank Dr. W. A. Beavers, this laboratory, for a sample of this material.

(31) Lightner, D. A.; Beavers, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 2677–2684.

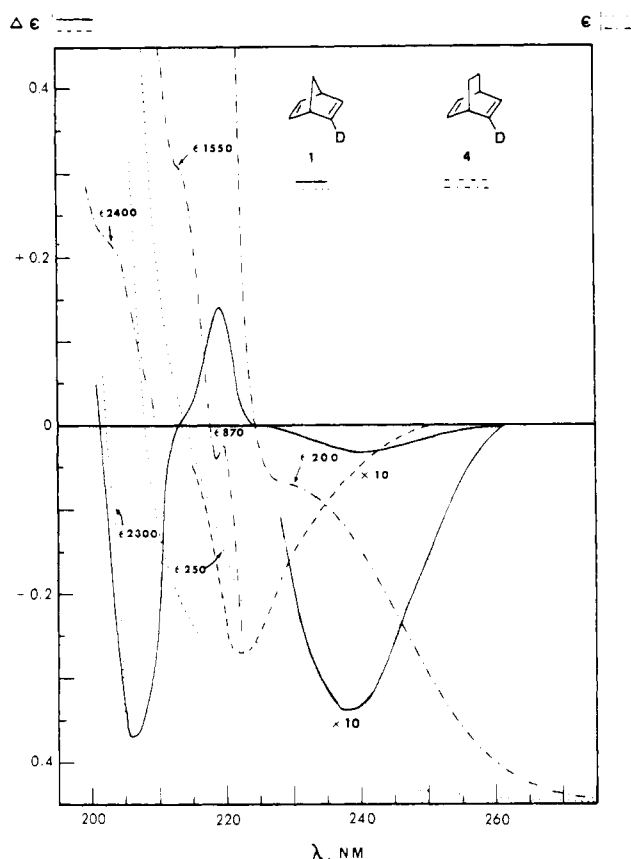
(32) Goring, H. L.; Towns, D. L. *J. Am. Chem. Soc.* **1963**, *85*, 2295–2298.

(33) Berson, J. A.; Willner, D. J. *J. Am. Chem. Soc.* **1962**, *84*, 675–676.

(34) We calculate a value of  $[\alpha]_D -492^\circ$  (isooctane) for 100% ee **13**. The value  $[\alpha]_D +265^\circ$  (isooctane) reported (ref 19) for the enantiomer of **13** of 40% ee apparently corresponds, rather, to 53.8% ee.

(35) Dallinga, G.; Toneman, L. H. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 805–812.

(36) Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2356–2363.

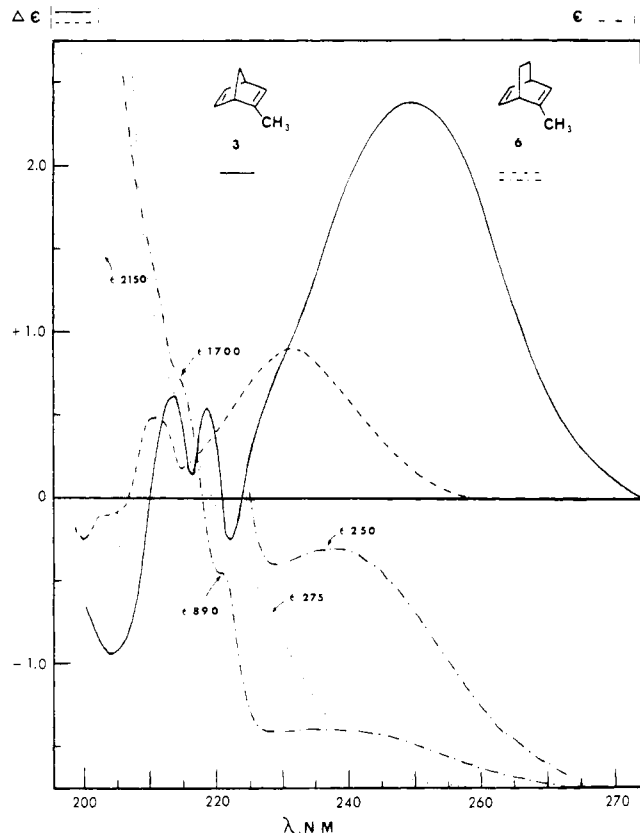


**Figure 1.** Circular dichroism (CD) and ultraviolet (UV) spectra of (1S)-2-deuteriobicyclo[2.2.1]hepta-2,5-diene (**1**) [CD, —; UV, .....] and (1S)-2-deuteriobicyclo[2.2.2]octa-2,5-diene (**4**) [CD, - - - - -; UV, .....] in *n*-heptane at 25 °C. CD data are corrected to 100% enantiomeric excess and 100%  $d_1$ . UV data are not scaled; relevant  $\epsilon$  values are indicated on the curves. The CD base lines (0) are the CD spectra of the  $d_0$  analogues, **2** and **5**.

Electronic interaction of the olefinic groups of **5** has been much less actively investigated. Dreiding models show a slightly larger dihedral angle ( $\theta = 120^\circ$ ) and longer 2-6 C-C bond distance (2.5 Å); hence, one is tempted to predict a weaker interaction in **5** than in **2**. That prediction is borne out in the UV data of Yamakawa and Kubota<sup>9</sup> for **5** (Table I), but those data also clearly show that **5** possesses electronic transitions not seen in the simple parent olefin, bicyclo[2.2.2]oct-2-ene. In a similar molecule, barrelene, SCF-CI calculations predict both through-space and through-bond interactions (mixing of  $\sigma$  and  $\pi$  orbitals) to contribute to the observed UV spectrum. Absorptions above 200 nm are attributed to the  $\pi$ - $\sigma^*$  type.<sup>37</sup>

Our UV data for **1** and **4** are shown in Table II and agree well with spectral data obtained by other workers. Spectra of the corresponding 2-methyl derivatives (**3** and **6**) show the expected bathochromic shifts of the excitations.

**Symmetric and Dissymmetric Chromophores.** In examining the optical activity of **1**, **3**, **4**, and **6**, it is helpful to recall the classification of chromophores into two limiting types: (1) inherently symmetric but dissymmetrically perturbed and (2) inherently dissymmetric.<sup>38,39</sup> This classification has proved to be useful in isolating and predicting the principal structural components contributing to the CEs of chiral molecules.<sup>40</sup> For example, the  $n$ - $\pi^*$  (+)-CE of dihydro-**9** is determined by the extrachromophoric perturbors, but the sign and much larger magnitude of the (-)-CE



**Figure 2.** Circular dichroism (CD) and ultraviolet (UV) spectra of (1S)-2-methylbicyclo[2.2.1]hepta-2,5-diene (**3**) [CD, —; UV, .....] and (1S)-2-methylbicyclo[2.2.2]octa-2,5-diene (**6**) [CD, - - - - -; UV, .....] in *n*-heptane at 25 °C. CD data are corrected to 100% enantiomeric excess. UV data are not scaled; relevant  $\epsilon$  values are indicated on the curves.

of **9** are dominated by the dissymmetric interactions of the carbonyl and olefin groups.<sup>19,28,31,39</sup>

The symmetrically disposed olefinic groups of **2** and **5** are sufficiently close to allow for interchromophoric interaction in a symmetric way. The resulting diene chromophores are symmetric, and the derived chiral structures **1**, **3**, **4**, and **6** fall into classification (1). Thus, chiral electronic transitions (CEs) associated with those structures necessarily arise only from extrachromophoric dissymmetric perturbation by the lone D or CH<sub>3</sub> group—unless the perturbors induce molecular distortion resulting in an inherently dissymmetric diene chromophore. We believe the contributions of the latter type are relatively unimportant. The CD spectra of **1**, **3**, **4**, and **6** therefore offer an additional way to detect new electronic transitions due to interaction of the olefin groups in **2** and **5**.

**Circular Dichroism Data.** The CD and UV spectra of **1** and **4** (Figure 1) and **3** and **6** (Figure 2) clearly show the advantage of obtaining both sets of data whenever possible, for the electronic transitions can be more clearly recognized in the CD spectra. Figure 1 provides evidence for three distinct near-UV electronic excitations in norbornadiene and one in bicyclo[2.2.2]octa-2,5-diene. These data (Table II) correlate particularly well with the UV data of Yamakawa and Kubota<sup>9</sup> (Table I). The expected geometry-dependent spectral shifts are recognizable and occur in the expected direction: the structures (**4**–**6**) with larger interchromophoric distances and dihedral angles ( $\theta$ ) exhibit less mixing and higher energy excitations. This is especially true of the long-wavelength excitations (which we assume correspond to the same type of transition) for **1** and **3** (and **4** and **6**) which shift to shorter wavelength in the bicyclo[2.2.2]octa-2,5-dienes (Table II).

Methyl perturbors greatly influence the electronic transitions of **2** and **4** as evidenced in Figure 2 and Table II. The multiplicity of transitions increases, the long-wavelength absorption maxima

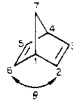

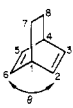

(37) Meyer, A. Y.; Pasternak, R. *Tetrahedron* **1977**, *33*, 3239–3241.

(38) Moffitt, W.; Moscovitz, A. *J. Chem. Phys.* **1959**, *30*, 648–660.

(39) For a discussion of this classification see: Deutsche, C. W.; Lightner, D. A.; Woody, R. W.; Moscovitz, A. *Annu. Rev. Phys. Chem.* **1969**, *20*, 407–448.


(40) See, for example, Lightner, D. A.; Jackman, D. E.; Christiansen, G. D. *Tetrahedron Lett.* **1978**, 4467–4470.

Table I. Experimental Electronic Transitions for Bicyclic Dienes and Olefins<sup>a</sup>

this work $\lambda$ (nm)	exptl data					
	Winstein <sup>5</sup> $\lambda$ (nm)	Yamakawa <sup>9</sup> $\lambda$ (nm)	Herman <sup>6</sup> $\lambda$	Robin <sup>7</sup> $\lambda$	Demeo <sup>b</sup> $\lambda$	Kupfermann <sup>c</sup> $\lambda$
 <b>2</b>						
230 sh (200)	230 (200)	231.2 (205)				237
220 sh (900)	200 (870)			221.1		
214 sh (1580)	214 (1480)	213.7 (1670)	211			
203 sh (2400)	205 (2100)	185.4 (7610)	188		206	208
		177.1 (7980)			182	181
					157	
 <b>3</b>						
	195			196	196	195
					168	168
 <b>5</b>						
220 sh (250)		218.0 (0.0058) <sup>d</sup>				
203 sh (2300)		197.8 (0.0360) <sup>d</sup>				
		175.4 (0.139) <sup>d</sup>				
 <b>6</b>						
		190.3 (7230)				

<sup>a</sup>  $\lambda$  in nm,  $\epsilon$  in  $M^{-1} cm^{-1}$ . <sup>b</sup> Demeo, D. A. Ph.D. Dissertation, University of California, Los Angeles, 1969. <sup>c</sup> Reference 14b. <sup>d</sup> Oscillator strength (*f*).

Table II. Circular Dichroism and Ultraviolet Spectral Data<sup>a</sup> for Bicyclic Dienes Measured in *n*-Heptane

 $(C+2)_n$ $R$	CD		UV	
	$R = D^b$ , $\lambda$ ( $\Delta\epsilon$ ) [ <i>R</i> ]	$R = CH_3$ , $\lambda$ ( $\Delta\epsilon$ ) [ <i>R</i> ]	$R = D$ , $\lambda$ ( $\epsilon$ )	$R = CH_3$ , $\lambda$ ( $\epsilon$ )
$n = 1$	237 (−0.032) [−0.066]	249 (+2.38) [+7.2] 222 (−0.25) [−0.46] 218.5 (+0.54) [+2.6] 213.5 (+0.62) [+4.7] 204 (−0.94) [−16]	230 sh <sup>d</sup> (200) 220 sh (870) 213 sh (1550) 202 sh (2400)	237 (250) 220 sh <sup>d</sup> (890) 213 sh (1700) 200 <sup>e</sup> (5200)
$n = 2$	222 (−0.027) [−0.041]	231 (+0.90) [+2.1] 211 (+0.48) [+0.33] 200 (−0.24) [−0.13]	220 sh <sup>d</sup> (250)	228 sh <sup>d</sup> (275)

<sup>a</sup>  $\lambda$  in nm,  $\epsilon$  and  $\Delta\epsilon$  in  $cm^{-1} M^{-1}$ , and *R* is the rotatory strength, value  $\times 10^{-40}$  cgs. <sup>b</sup> No change in CD spectrum in 1:1 heptane-ethanol. <sup>c</sup> In ethanol:  $\epsilon_{236}^{sh}$  255,  $\epsilon_{220}^{sh}$  970,  $\epsilon_{213}^{sh}$  1830 for 2-methylbicyclo[2.2.2]octa-2,5-diene. <sup>d</sup> sh = shoulder. <sup>e</sup> Not maximum.

shift to longer wavelengths (cf. Figure 1), and the CD bands become more intense. Since the corresponding UV intensities remain relatively unchanged (for **3** and **6** vs. **1** and **4**), methyl perturbors induce a greater magnetic dipole transition moment.

**Theoretical Considerations.** We have chosen to examine the UV and CD spectra of **1** in some theoretical detail, in order to indicate a basis for understanding the spectra of related compounds. Compound **1** is small enough (36 valence electrons) to allow an ab initio (STO-4G) treatment of the ground-state molecular orbitals.<sup>41</sup> The low-lying spin-singlet electronic transitions were determined by using the localized orbital RPA (LORPA) method that is described elsewhere in detail.<sup>42,43</sup> The effect of

deuterium substitution was treated by assuming a slightly shortened C–D bond length relative to a C–H bond.<sup>2a,b</sup>

The experimental geometry of norbornadiene<sup>36</sup> was used in the calculations, except that the C–D bond was taken to be 0.01 Å shorter than the corresponding C–H bond; this bond-length shortening, while slightly exaggerated, ensures that the qualitative features of the induced chirality are reproduced in the calculations. The standard minimal STO-4G basis set was used as provided in the GAUSSIAN 70 program system, yielding a total SCF energy of −268.322 696 6 au. The MOs were then localized according to our modified Foster–Boys–Coffey procedure,<sup>42</sup> and the full set of 324 valence-shell singly excited configurations was used in the LORPA calculation; the effects of all the corresponding double excitations are included automatically by the RPA procedure.<sup>44</sup>

(41) Hehre, W. J., et al. QCPE 236, Quantum Chemistry Program Exchange.

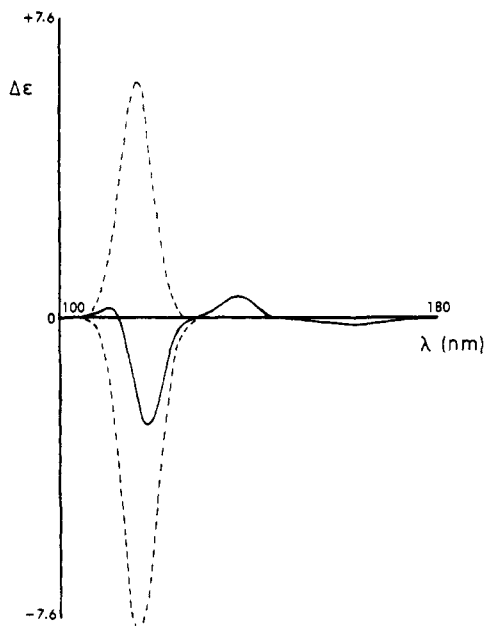
(42) Bouman, T. D.; Voigt, B.; Hansen, Aa. E. *J. Am. Chem. Soc.* **1979**, *101*, 550–558.

(43) Hansen, Aa. E.; Bouman, T. D. *Adv. Chem. Phys.*, **1980**, *44*, 545–644.

**Table III.** Calculated Electronic Transitions for Deuterionorbornadiene (1) in an ab Initio Localized Orbital RPA Model

excitation	$\Delta E (\lambda_{\max})^a$	$f^{\text{osc}}^a$	$R[r]^a$	% LE <sup>a</sup>	% CT <sup>a</sup>
1. $^1A_2$	7.67 (162)	~0	-0.22	72.6	22.7
2. $^1B_2$	9.06 (137)	0.13	+0.89	58.4 <sup>b</sup>	19.0 <sup>b</sup>
3. $^1A_2$	9.70 (128)	0	0	c	
4. $^1B_2$	9.93 (125)	0.13	+0.05	77.9	21.9
5. $^1B_2$	10.71 (116)	0.04	-14.35	60.4	29.8
6. $^1B_1$	10.79 (115)	0.01	+10.71	81.1	14.7

<sup>a</sup> Energies in eV,  $\lambda$  nm;  $f^{\text{osc}}$  is the energy-free mixed oscillator strength,  $R[r]$  is the energy-free, origin-independent rotatory strength (ref 42), units are cgs  $\times 10^{40}$ ; LE = locally excited, CT = charge-transfer contributions (see text). <sup>b</sup> Bridge contributions into the two  $\pi^*$  orbitals total 13.9%. <sup>c</sup> Not analyzed.



**Figure 3.** Simulation of CD spectrum (—) of **1** from calculated energies and rotatory strengths. Each band is represented by a Gaussian shape, with the half-width  $\Delta\lambda^\circ$  of the long-wavelength band assigned as 8 nm, and 5 nm assumed for the other bands.  $\Delta\epsilon^\circ$  for each band is computed from  $\Delta\epsilon^\circ = R\lambda^\circ/40.5\Delta\lambda^\circ$ . The dashed lines (---) show that two calculated, overlapping, oppositely signed bands add together to give the observed (—) spectrum in the short-wavelength region.

Our calculated results for the lowest electronic transitions are shown in Table III. As is typical of minimal basis set ab initio calculations, the excitation energies are somewhat too high. However, the simulated CD spectrum shown in Figure 3 indicates that the ordering of the states and the calculated relative intensities are not unreasonable. Our use of localized orbitals allows us to decompose the excitation eigenvectors and transition moments into "locally excited" and "charge-transfer" contributions. Here "locally excited" means the set of configurations involving all promotions within the set of six ethylene-like bonds ( $\sigma$  as well as  $\pi$ ) on each olefinic group. "Charge transfer" means all configurations involving promotion from one such set to the other.

Table III shows that charge transfer is present in all the low-lying excitations to the extent of 15–30%, while the methylene bridge and bridgehead hydrogens play a significant role only in excitation no. 2, where their contribution can be described as hyperconjugation. Excitation 1 is assigned as a forbidden,  $^1A_1 \rightarrow ^1A_2$  band resulting predominantly from the out-of-phase coupling of the two local  $\pi \rightarrow \pi^*$  excitations, with a substantial out-of-phase charge transfer contribution. We identify this excitation with the observed (–) CE at 237 nm, and with the  $N \rightarrow V_1$  (valence-shell) assignment of Kuppermann's group.<sup>14b</sup> The second band is computed to be an allowed  $^1A_1 \rightarrow ^1B_2$  excitation consisting

of the in-phase coupling of local and charge-transfer  $\pi \rightarrow \pi^*$  excitations, including, as indicated above, hyperconjugation across the bridge. This band is to be identified with the (+) CE seen at 216 nm, and with an  $N \rightarrow V_2$  assignment;<sup>14b</sup> however, our calculations do not permit an assessment of the Rydberg part of this band.<sup>7,8</sup> A Rydberg transition in this region appears not to contribute significantly to the CD spectrum near 216 nm. The third computed transition is forbidden  $^1A_1 \rightarrow ^1A_2$ , and is also essentially optically inactive. The fourth excitation,  $^1A_1 \rightarrow ^1B_2$ , is allowed but only weakly optically active, and is similar in nature to the second transition, except that bridge contributions are unimportant, and there is substantial  $\sigma(C=C) \rightarrow \pi^*$  participation. The negative CE seen at 205 nm can be associated with the superposition and near-cancellation of excitations 5 and 6; excitation 5 is a coupling of local  $\sigma(C=C) \rightarrow \pi^*$  excitations with  $\pi \rightarrow \pi^*$  charge-transfer terms, while excitation 6 is predominantly a coupling of local  $\sigma \rightarrow \pi^*$  ("n- $\pi^*$ -like") excitations. Kuppermann's data<sup>14b</sup> show a peak which includes the 205–216-nm region. We find no evidence of low-lying  $\pi \rightarrow \sigma^*$  excitations.<sup>15</sup>

It is clear that our minimal basis treatment cannot account for possible Rydberg states, and the computed valence-shell excitation energies are uniformly too high. Our experience, however, is that additional basis functions serve mainly to lower the energies, with little effect on the computed transition moments. Our use of the energy-free oscillator and rotatory strength quantities  $f^{\text{osc}}$  and  $R[r]$  further lessens the importance of additional basis functions.<sup>42,43</sup> On the basis of the overall agreement between the simulated and experimental CD spectra, we believe that LORPA calculations of UV and CD spectra can provide useful insights into the electronic structure of chiral systems, particularly those systems made chiral by isotopic substitution.

## Experimental Section

**General.** Circular dichroism spectra were recorded on a JASCO J-40A instrument equipped with a photoelastic modulator, ultraviolet spectra were recorded on a Cary 219 spectrophotometer, and sodium D-line rotations were determined on a Perkin-Elmer 141 polarimeter. All nuclear magnetic resonance spectra (60 MHz) were determined on a Perkin-Elmer R-24B instrument, mass spectra were recorded at 70 eV on a JEOL JMS-07 spectrometer, and infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer. All melting points are uncorrected and were determined on a Thomas-Hoover apparatus. Gas chromatography (GC) was performed on a Varian Aerograph 2400 (analytical) using column A (6 ft  $\times$  1/8 in., 5% FFAP on Chromosorb W AW-DMCS) or 1720 (preparative) instrument using column B (6 ft  $\times$  3/8 in., 12% QF-1 on Chromosorb W), column C (6 ft  $\times$  3/8 in., 5% SE-30 on Chromosorb W AW-DMCS), or column D (8 ft  $\times$  3/8 in., 15% Carbowax 20M on Chromosorb W AW-DMCS). Combustion analyses were performed by Chemalytics, Tempe, Ariz. Spectral data were obtained by using spectral-grade solvents (MCB). Other solvents were distilled and dried before use: diethyl ether and tetrahydrofuran (from  $LiAlH_4$ ) and dichloromethane (from  $P_2O_5$ ) were used freshly distilled or stored over 4 Å molecular sieves. Tetramethylethylenediamine (TME-DA) (Aldrich) was distilled twice from  $CaH_2$  and stored over 5 Å molecular sieves. Chromatography was accomplished on Florisil (Floridin Co.), Merck silica gel, or Merck neutral alumina.

**(1S)-Bicyclo[2.2.1]hept-5-en-2-one (9).**<sup>19,22</sup> Norbornenyl acetate (7, 1.012 g, 6.65 mmol,  $[\alpha]_D^{25} -23.965^\circ$  corresponds to 48% ee<sup>27</sup>), prepared by asymmetric hydroboration of norbornadiene with diisopinocampheylborane<sup>18,19</sup> in 6 mL of dry diethyl ether, was added dropwise to a suspension of 0.19 g (5 mmol) of  $LiAlH_4$  in 14 mL of dry ether. Stirring at room temperature was continued for 8 h after addition was complete. Then the mixture was treated carefully at ice-bath temperature with 4 mL of 3 N aqueous NaOH and the ether layer separated. The aluminum salts were washed twice with ether, and the combined extracts were dried ( $MgSO_4$ ) and evaporated at reduced pressure (ethanol!) to give 703 mg (96%) of colorless, solidified *exo*-bicyclo[2.2.1]hept-5-en-2-ol, pure by GC on column A, 100 °C. The alcohol (677 mg, 6.25 mmol) was dissolved in 20 mL of  $CH_2Cl_2$  and treated under  $N_2$  with 2.03 g (9.4 mmol) of the Corey reagent (pyridinium chlorochromate<sup>20</sup>). After 1 h (reaction monitored by GC on column A) another 0.5-g portion of the oxidant was added and the mixture was stirred for an additional 5-h period. Filtration through Florisil and evaporation of the solvents gave the crude product (0.8 g). Distillation at 105 °C (20 mmHg) afforded 230 mg of the product, having the same GC retention time (column A) as authentic material.<sup>22,31</sup> It was 70% pure by UV ( $\lambda_{\max}$  307 nm in hexane),<sup>19,22,28</sup>  $[\alpha]_D^{25} -550^\circ$  (hexane) (48% ee). The yield was 24%,

the residue being higher boiling (polymeric?) material.

**(1S)-Bicyclo[2.2.1]hept-5-en-2-one *p*-Toluenesulfonylhydrazide (10).** The ketone prepared above (230 mg) and *p*-toluenesulfonylhydrazide (300 mg, 1.2 molar excess) were dissolved in 2 mL of CH<sub>3</sub>OH and left at room temperature for 24 h. After cooling at 0 °C, the crystalline tosylhydrazide was removed by filtration and washed with ether–pentane to give 320 mg (85%) of product, mp 182–183 °C dec (with previous darkening),  $[\alpha]_D -124^\circ$  (c 1.7, CHCl<sub>3</sub>).

To determine that the ee had not been altered by crystallization, a sample of tosylhydrazide (69.1 mg, 0.25 mmol) was dissolved in a mixture of 3.5 mL of acetone and 1 mL of H<sub>2</sub>O. The solution was cooled in an ice bath, then 178 mg (1 mmol) of *N*-bromosuccinimide was added with stirring, and stirring was continued for 2 min. Two milliliters of 0.5 M aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> was added, followed by 2.5 mL of H<sub>2</sub>O, and the reaction mixture was extracted with ether. The extracts were washed with 1 N aqueous NaHCO<sub>3</sub> and saturated aqueous NaCl, dried (MgSO<sub>4</sub>), and evaporated at room temperature. The crude oily product (36.6 mg) was purified by preparative GC on column B, 80 °C, to give a sample having identical properties with those of the starting ketone and  $[\alpha]_D -550^\circ$  (hexane) corresponding to 48% ee.

Racemic tosylhydrazide was prepared from racemic 5-norbornen-2-one (0.492 g, 4.55 mmol) and *p*-toluenesulfonylhydrazide (0.847 g, 4.55 mmol) which were gently warmed to dissolve in 4 mL of CH<sub>3</sub>OH and left at room temperature for 8 h. After cooling to 0 °C, the crystals were collected by filtration and washed with CH<sub>3</sub>OH to give 1.13 g (90%) of product, mp 185–187 °C dec. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH gave material with mp 188–190 °C dec. The tosylhydrazide had IR (Nujol) 3220, 3075, 1670, 1600, 1330, 1170 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>)  $\delta$  1.4–2.1 (m, 4 H, 2 CH<sub>2</sub>), 2.39 (s, 3 H, ArCH<sub>3</sub>), 3.04 (br s, 1 H, CH), 3.25 (br s, 1 H, CH), 6.00 and 6.20 (m, 2 H, vinyl H), 7.22 and 7.75 (d, *J* = 8 Hz, 2 × 2 H ArH); MS *m/e* 276 [M<sup>+</sup>], 121 [M – Ts], 91 (100%). Anal. Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub>S: C, 60.84; H, 5.84; N, 10.14. Found: C, 61.09; H, 5.66; N, 10.47.

**(1S)-2-Deuteriobicyclo[2.2.1]hepta-2,5-diene (1).**<sup>45</sup> The tosylhydrazide 10 (553 mg, 2.0 mmol, 48% ee) was suspended in 4 mL of anhydrous TMEDA and treated under N<sub>2</sub> at –65 °C with 5.5 mL of 1.6 M CH<sub>3</sub>Li (4.4 equiv). When allowed to warm up to room temperature the mixture gave a deep red solution. After 1 day at room temperature the reaction solution was cooled to –30 °C, then treated with 0.25 mL of 99.8% D<sub>2</sub>O and allowed to warm to room temperature to give an almost colorless reaction mixture. This was extracted with pentane–H<sub>2</sub>O and the organic layer washed with 2 N aqueous HCl followed by 3 M aqueous NaOH. It was dried (MgSO<sub>4</sub>), filtered through silica gel, and concentrated by efficient column distillation from a water bath (40–50 °C). The product was separated by preparative GC on column C, 55 °C, to give the 99.9% pure, highly volatile product in 25% yield. It had CD (*n*-heptane and 1:1 heptane–ethanol)  $\Delta\epsilon_{237} = -0.032$  (100% ee); UV (*n*-heptane)  $\epsilon_{230}^{sh}$  200,  $\epsilon_{220}^{sh}$  870,  $\Delta\epsilon_{213}^{sh}$  1550,  $\epsilon_{202}^{sh}$  2400; NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.99 (t, 2 H, CH<sub>2</sub>), 3.58 (septet, 2 H, CH), 6.70 (t, *J* = 2 Hz, 3 H, =CH); MS, *m/e* 93 [M<sup>+</sup>], 92 (100%). The diene was 99% *d*<sub>1</sub> by MS.

**Bicyclo[2.2.1]hepta-2,5-diene (Norbornadiene, 2).** Commercial material (Aldrich) was purified by careful preparative GC on column D, 60 °C, to give a sample which was >99.9% pure by analytical GC on column A. It had UV (*n*-heptane)  $\epsilon_{230}^{sh}$  200,  $\epsilon_{220}^{sh}$  900,  $\epsilon_{214}^{sh}$  1580,  $\epsilon_{203}^{sh}$  2400; NMR<sup>46</sup> (CCl<sub>4</sub>)  $\delta$  1.91 (m, 2 H, CH<sub>2</sub>), 3.47 (m, 2 H, 2 CH), 6.56 (m, 4 H, =CH); MS<sup>47</sup> *m/e* 92 [M<sup>+</sup>], 91 (100%), 66 [M – C<sub>2</sub>H<sub>2</sub>].

**(1S)-2-Methylbicyclo[2.2.1]hepta-2,5-diene (3).**<sup>48</sup> The reaction was essentially the same as for the preparation of 1 except that excess (5 equiv) CH<sub>3</sub>I (filtered through activity III Al<sub>2</sub>O<sub>3</sub>, neutral) was used to quench the lithium salt at –60 °C in place of D<sub>2</sub>O. The 99.9% pure diene was isolated following repeated preparative GC on column D, 70 °C. It had CD (*n*-heptane)  $\Delta\epsilon_{249} = +2.38$  (100% ee), (95% ethanol)  $\Delta\epsilon_{249} = +2.41$ ; UV (*n*-heptane)  $\epsilon_{237}^{sh}$  250,  $\epsilon_{220}^{sh}$  890,  $\epsilon_{213.5}^{sh}$  1700,  $\epsilon_{200}^{sh}$  5200 (not max); NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.87 (d, *J* = 1.5 Hz, 3 H, CH<sub>3</sub>), 2.0 (m, 2 H,

CH<sub>2</sub>), 3.23, 3.51 (m, 1 H, CH), 6.08 (m, 1 H, =CH), 6.73 (m, 2 H, =CH); MS *m/e* 106 [M<sup>+</sup>], 105 [M – H], 91 (100%), 66 [M – C<sub>3</sub>H<sub>4</sub>].

**(1S)-Bicyclo[2.2.2]oct-5-en-2-one (13).**<sup>31</sup> (1S)-endo-Bicyclo[2.2.2]oct-5-en-2-ol<sup>30</sup> (0.68 g, 5.07 mmol,  $[\alpha]_D^{CHCl_3} -56^\circ$ , 76% ee<sup>34</sup>) was dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> and oxidized with 3 g (ca. 2 equiv) of pyridinium dichromate.<sup>23</sup> After the mixture was stirred at room temperature for 24 h, 95% of the alcohol was oxidized, according to GC column A, 90 °C. The reaction mixture was diluted with pentane–ether and filtered through Florisil–MgSO<sub>4</sub>. The colorless solution was evaporated to give an oil which was redissolved in 50 mL of pentane and washed with 2 N aqueous HCl (to remove traces of pyridine) and saturated aqueous NaCl. The UV<sup>31,49</sup> of the pentane solution showed that it contained 61% (0.41 g) of the ketone,  $[\alpha]_D -370^\circ$  (c 0.82, pentane). Evaporation of the solvent left 0.675 g of a colorless oil.

A sample of racemic bicyclo[2.2.2]oct-5-en-2-one was prepared from racemic endo-bicyclo[2.2.2]oct-5-en-2-yl acetate<sup>50</sup> ((±)-11) first by LiAlH<sub>4</sub> hydrolysis of the acetate by the method described for the preparation of 8. Oxidation of the racemic alcohol ((±)-12) was conducted as above for the synthesis of 13.

**(1S)-Bicyclo[2.2.2]oct-5-en-2-one *p*-Toluenesulfonylhydrazide (14).** The 1S ketone 13 prepared above (0.675 mg total mixture) was dissolved in 6 mL of CH<sub>3</sub>OH and treated with 1 g (excess) of *p*-toluenesulfonylhydrazide. After heating briefly, the solution was left at room temperature for 24 h to crystallize. The mixture was cooled to 0 °C and filtered. The crystals were washed with CH<sub>3</sub>OH and ether to give 0.82 g (84%) of product, mp 215–216 °C dec. It had IR (Nujol) 3220, 3060, 1650, 1600, 1330, 1165 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>)  $\delta$  1.2–1.8 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 1.97 (br d, 2 H, CH<sub>2</sub>), 2.39 (s, 3 H, ArCH<sub>3</sub>), 2.87, 3.23 (m, 1 H, CH), 6.12, 6.22 (2 t, *J* = 2 Hz, 2 H, =CH);  $[\alpha]_D -84^\circ$  (c 1.2, CHCl<sub>3</sub>). A sample of racemic tosylhydrazide ((±)-14) was prepared as above from racemic ketone ((±)-13) and had mp 223–224 °C dec after crystallization from CHCl<sub>3</sub>–CH<sub>3</sub>OH.

Anal. Calcd for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O<sub>5</sub>S: C, 62.04; H, 6.25; N, 9.65. Found: C, 62.21; H, 6.08; N, 9.85.

The optically active tosylhydrazide 14 could be converted back to starting optically active ketone of the same, original ee by the NBS method described for 10.

**(1S)-2-Deuteriobicyclo[2.2.2]octa-2,5-diene (4).** The reaction was carried out according to the procedure used for synthesis of 1. Thus, a 406-mg (1.4 mmol) sample of 14 in 3 mL of TMEDA was reacted with 4 mL of 1.6 M CH<sub>3</sub>Li (4.5 equiv) in ether and quenched with 0.2 mL of 99.8% D<sub>2</sub>O to give 100 mg (67%) of a 99.9% pure, colorless, crystalline product (mp 55 °C) after preparative GC on column D, 90 °C. It had CD (*n*-heptane)  $\Delta\epsilon_{222} = -0.027$  (100% ee); UV (*n*-heptane)  $\epsilon_{220}^{sh}$  250; NMR (CDCl<sub>3</sub>)  $\delta$  1.23 (t, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 3.56 (m, 2 H, 2 CH), 6.19 (t?, *J* = 3.6 Hz, 3 H, =CH); MS *m/e* 107 [M<sup>+</sup>], 79 [M – C<sub>2</sub>H<sub>4</sub>] (100%), 78. Mass spectral and NMR analysis indicated that the sample of 4 was 96% *d*<sub>1</sub> and 4% *d*<sub>0</sub>.

**Bicyclo[2.2.2]octa-2,5-diene (5).**<sup>51</sup> Racemic tosylhydrazide ((±)-14) was treated as above to give the crystalline diene (mp 55–56 °C) after preparative GC on column D, 90–100 °C. It had UV (*n*-heptane)  $\epsilon_{220}^{sh}$  250,  $\epsilon_{203}^{sh}$  2300; NMR<sup>51</sup> (CDCl<sub>3</sub>)  $\delta$  1.23 (t, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 3.54 (m, 2 H, 2 CH), 6.20 (t?, *J* = 3.6 Hz, 4 H, =CH); MS<sup>47</sup> *m/e* 106 [M<sup>+</sup>], 78 (M – C<sub>2</sub>H<sub>4</sub>) (100%).

**(1S)-2-Methylbicyclo[2.2.2]octa-2,5-diene (6).** The reaction was carried out according to the procedure developed for the synthesis of 3. Thus, 400 mg (1.38 mmol) of 14 in 3 mL of TMEDA was reacted with 3.9 mL of 1.6 M CH<sub>3</sub>Li (4.5 equiv) in ether and quenched with 0.8 mL (12.5 mmol) of CH<sub>3</sub>I as before. Workup and preparative GC on Column 3, 100 °C, gave separated 6 from 5 (93:7) to give 104 mg (63%) of 99.9% pure, oily 6. It had CD (*n*-heptane)  $\Delta\epsilon_{231} = +0.90$  (100% ee); UV (*n*-heptane)  $\epsilon_{228}^{sh}$  275; NMR (CDCl<sub>3</sub>)  $\delta$  1.23 (t, 4 H, CH<sub>2</sub>), 1.76 (d, *J* = 1.8 Hz, 3 H, CH<sub>3</sub>), 3.3 (br m, 2 H, CH), 5.73 (m, 1 H, =CH), 6.20 (t, *J* = 3.8 Hz, 2 H, =CH); MS *m/e* 120 [M<sup>+</sup>], 105 [M – CH<sub>3</sub>], 92 [M – C<sub>2</sub>H<sub>4</sub>] (100%), 91.

**Acknowledgments.** D.A.L. and J.K.G. thank the National Science Foundation (CHE 76-08759) for generous support of this work. T.D.B. thanks the Graduate School of Southern Illinois University, Edwardsville, for support in the form of a research scholar award.

(49) Geribaldi, S.; Torri, G.; Azzaro, M. *Bull. Soc. Chim. Fr.* **1973**, 2836–2838.

(50) Prepared by the Diels–Alder reaction of 1,3-cyclohexadiene with vinyl acetate (ref 31). We thank Mr. Stephen Handler, this laboratory, for preparing (±)-11.

(51) Muller, E. *Chem. Ber.* **1976**, 109, 3793–3803.

(45) Racemic 2-deuterionorbornadiene has been prepared by prolonged reaction of *n*-butyllithium with norbornadiene followed by D<sub>2</sub>O quenching: Streitwieser, Jr., A.; Caldwell, R. A. *J. Org. Chem.* **1962**, 27, 3360–3361.

(46) In agreement with Tori, K.; Hata, Y.; Muneyuki, T.; Takano, T.; Tsuji, T.; Tanida, H. *Can. J. Chem.* **1964**, 42, 926–933.

(47) In agreement with Goto, T.; Tatematsu, A.; Hata, Y.; Muneyuki, R.; Tanida, H.; Tori, K. *Tetrahedron* **1966**, 22, 2213–2222; “CRC Atlas”, Vol. II, 52.5.

(48) Racemic 2-methylnorbornadiene has been obtained by reacting norbornadiene with *n*-butyllithium and quenching the vinyl anion with CH<sub>3</sub>I: Jefford, C. W.; Rimbault, C. G. *J. Org. Chem.* **1978**, 43, 1908–1922. Mas-kornick, M. J. *Tetrahedron Lett.* **1972**, 1797–1800. The latter author showed that 2-methylnorbornadiene is base sensitive toward isomerization to 5-methylenbicyclo[2.2.1]hept-2-ene.