

the 1,2 and 3,4 adducts from the 1,4 adducts and all the adducts from the dimers.

The adduct (4.3 g) was prepared from chlorotrifluoroethylene (5 g) and *trans*-pentadiene (3 ml). Dechlorination in the same manner as for the *cis* case consumed all the starting material. The product isomers were obtained pure for nmr spectra by preparative glpc.

**Structure of the *trans*-1,3-Pentadiene-Trifluoroethylene 1,4 Cycloadducts.** Fractions 8 and 9 of Table IV were obtained free of the other components by preparative vapor chromatography. The mixture of these two components (75 mg) was added to a solution containing 131 mg of potassium *tert*-butoxide in 1.6 ml of *tert*-butyl alcohol. The solution was refluxed for 1.5 hr, diluted with water, and extracted with pentane. The pentane extract was washed four times with 5-ml portions of water, dried over calcium chloride, decanted, and concentrated with a 10-cm bead-packed column. The fluorotoluene peak was collected by preparative glpc and examined as a carbon tetrachloride solution by glpc and

infrared analysis. The infrared spectrum was compared with those obtained from a series of solutions prepared in an analogous manner to those used in the study of the aromatization products from the isoprene cycloadducts. This analysis showed that the *o*-fluorotoluene contributes less than 10% to the fluorotoluene mixture. Glpc analysis (22 ft MNPN) indicates a ratio of *o*- to *m*-fluorotoluene of 1:19.

**Addition of Chlorotrifluoroethylene to Dienes.** Hydroquinone (~50 mg) was placed in a heavy-walled Pyrex tube cooled to  $-80^{\circ}$  with a Dry Ice-acetone bath and the amounts of diene and chlorotrifluoroethylene indicated in Table IX were added.

**Acknowledgment.** We gratefully acknowledge support of this research by grants from the National Science Foundation and the National Institutes of Health. L. E. W. thanks the National Institutes of Health for a postdoctoral fellowship.

## Stereochemistry of the Noncatalytic Addition of Molecular Deuterium to Cyclopentadiene<sup>1</sup>

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**Abstract:** The noncatalytic reaction of deuterium gas with cyclopentadiene at  $300^{\circ}$  is found by nmr spectroscopy to give both *cis*-3,5-dideuteriocyclopentene and undeuterated cyclopentene. With deuterons and olefinic protons decoupled, the proton spectrum of *cis*-3,5-dideuteriocyclopentene is analyzed as an A<sub>2</sub>BC system where the A protons are on C<sub>2</sub> and C<sub>5</sub> and the BC protons are on C<sub>4</sub>. The following parameters are obtained:  $\delta_A = 2.282$  ppm,  $\delta_B = 1.797$  ppm,  $\delta_C = 1.808$  ppm,  $J_{AB}(\text{trans}) = 5.63$  Hz,  $J_{AC}(\text{cis}) = 9.46$ ,  $J_{BC}(\text{gem}) = -12.74$  Hz. The difference ( $0.012 \pm 0.002$  ppm) between  $\delta_B$  and  $\delta_C$  represents a real stereochemical isotope-effect chemical shift. The formation of undeuterated cyclopentene is ascribed to a concerted Woodward-Hoffmann allowed suprafacial transfer of two hydrogen atoms from *cis*-3,5-dideuteriocyclopentene to cyclopentadiene. The stereochemistry of the deuterated cyclopentene is in agreement with a concerted suprafacial 1,4 addition of molecular deuterium to cyclopentadiene.

The thermal, noncatalytic eliminations of molecular hydrogen from 1,4-cyclohexadiene<sup>3</sup> and cyclopentene<sup>4</sup> to give benzene and cyclopentadiene, respectively, appear to be concerted reactions obeying the Woodward-Hoffmann rules.<sup>5</sup> Baldwin<sup>4c</sup> has shown that both 1,2 and 1,4 eliminations of hydrogen from cyclopentene take place at  $550^{\circ}$ , and that 1,4 elimination is favored over 1,2 elimination by a factor of 6. It has also been observed that molecular hydrogen can add to cyclopentadiene in an uncatalyzed reaction to give cyclopentene.<sup>4d</sup> Only in the cyclohexadiene case,<sup>3d,e</sup> however, has the stereochemistry of the addition or elimination of molecular hydrogen been determined. In the present work, we have studied the uncatalyzed

addition of molecular deuterium to cyclopentadiene as a means of determining the stereochemistry of the reaction.

### Results and Discussion

The reaction of cyclopentadiene with a large excess of deuterium gas at a pressure of about 40 atm (measured at room temperature) was carried out in a stainless-steel vessel containing phenothiazine at  $300^{\circ}$  for 4.5 hr. Experiments with hydrogen gas showed that the presence of phenothiazine effectively inhibited hydrogenation reactions catalyzed by the walls of the vessel, and completely prevented the formation of cyclopentane. At  $300^{\circ}$ , the hydrogenation was effectively irreversible.

The cyclopentene fraction was isolated by vpc from the volatile reaction product of the cyclopentadiene-deuterium reaction, and its 100-MHz proton spectrum was obtained under (i) normal conditions, (ii) with the deuterons decoupled, and (iii) with both the deuterons and the olefinic protons decoupled (Figure 1). Only the spectrum taken under condition iii will be discussed in detail.

The most likely structure for the "deuterated cyclopentene" is *cis*-3,5-dideuteriocyclopentene (1).

(1) This work was supported by USPHS Grant No. GM12769.

(2) Holder of an Otan fellowship.

(3) (a) R. J. Ellis and H. M. Frey, *J. Chem. Soc. A*, 553 (1966); (b) S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, 63, 985 (1967); (c) S. W. Benson and R. Shaw, *J. Amer. Chem. Soc.*, 89, 5351 (1967); (d) H. M. Frey, A. Krantz, and I. D. R. Stevens, *J. Chem. Soc. A*, 1734 (1969); (e) I. Fleming and E. Wildsmith, *Chem. Commun.*, 223 (1970).

(4) (a) D. W. Vanas and W. D. Walters, *J. Amer. Chem. Soc.*, 70, 4035 (1948); (b) H. Tanji, M. Uchiyama, A. Amano, and H. Tokuhisa, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, 70, 307 (1967); (c) J. E. Baldwin, *Tetrahedron Lett.*, 2953 (1966); (d) C. J. Grant and R. Walsh, *Chem. Commun.*, 667 (1969).

(5) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 141.

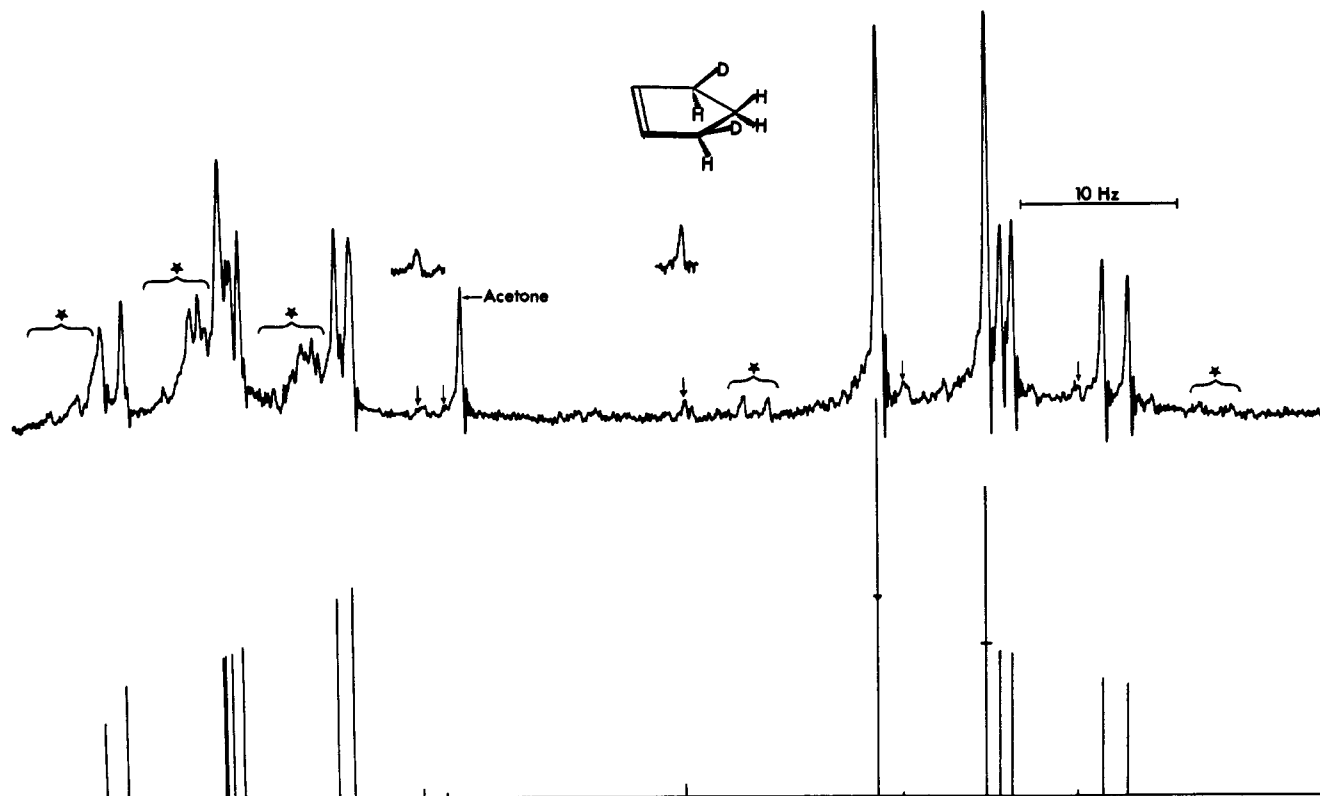
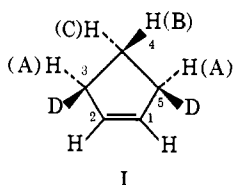


Figure 1. Nmr spectrum (100 MHz) of the reaction product of cyclopentadiene with deuterium. The deuterons are decoupled and the olefinic protons are also decoupled and not shown. Lines marked with asterisks belong to cyclopentene. The arrows point to weak lines which can be easily observed at high rf levels (*e.g.*, see upper central portion of the spectrum). The stick plot at the bottom is calculated from the parameters given in Table II.



The proton spectrum of I under condition iii mentioned above is expected to be of the  $A_2BC$  type, where the A protons are those on  $C_3$  and  $C_5$ , and the B and C protons are those on  $C_1$ . The chemical shift difference between the B and C protons is expected to be very small, being due only to a stereochemical isotopic effect of the deuterons. On the other hand, the chemical shift difference between the A protons and either the B or C proton should be relatively large, as the A protons are allylic whereas the B and C protons are homoallylic. In fact, the proton spectrum of cyclopentene itself clearly shows the allylic protons to be less shielded than the homoallylic methylene protons by about 0.5 ppm (*i.e.*, 50 Hz at 100 MHz).

The spectrum in Figure 1, however, is too complex for the  $A_2BC$  system expected from I. An examination shows that lines marked with an asterisk belong to cyclopentene itself and not to any deuterated cyclopentene. The remaining lines then can be satisfactorily assigned to the deuteriocyclopentene I, as will be shown subsequently. There are a number of weak lines, whose positions are shown by arrows in Figure 1, that have insufficient signal-to-noise ratios for detection when the strong lines are observed in an unsaturated state. An increase in radio-frequency power, although leading to saturation of the strong lines, does increase

the weak lines, as shown in Figure 1, since these latter lines correspond to nearly forbidden transitions and do not saturate easily.<sup>6</sup> This procedure also serves to distinguish between such nearly forbidden transitions and allowed transitions of possible traces of impurities.<sup>6</sup> Altogether 21 lines were identified as belonging to I and were used in the spectral analysis.

Trial calculations of  $A_2BC$  spectra with  $\Delta\nu_{AB} = 50$  Hz,  $\Delta\nu_{BC} = 0$  Hz,  $J_{BC} = -12$  Hz,  $J_{AB} = 6$  Hz,  $J_{AC} = 9$  Hz, allowed an assignment of the observed signals to be made. The value of  $J_{AA}$  does not affect the spectrum of an  $A_2BC$  system and therefore also cannot be obtained from the present work. Iterative calculations keeping  $\Delta\nu_{BC} = 0$  did not lead to a satisfactory solution; in particular lines 9 and 10 (see Table I) were calculated to be well separated rather than the two virtually coincident transitions needed to fit the experimental spectrum. When  $\Delta\nu_{BC}$  was allowed to vary, an excellent agreement was obtained both in line positions and intensities of the observed and calculated spectra (Figure 1 and Table I). Since  $\Delta\nu_{BC}$  represents an isotope chemical-shift effect which is differential in character, *i.e.*, the effect of two deuterons *cis* to a vicinal proton *vs.* the corresponding *trans* situation, a careful examination was made of possible errors in  $\Delta\nu_{BC}$ . As stated before,  $\Delta\nu_{BC}$  is clearly not zero; with a value of  $\Delta\nu_{BC}$  of 1.2 Hz as found in the iterative procedure, it was found that a small change in  $\Delta\nu_{BC}$  (*e.g.*  $\pm 0.2$  Hz), keeping  $\nu_B + \nu_C$  constant, also led to a reasonable fit, but a lowering of  $\Delta\nu_{BC}$  to 0.8 Hz resulted in an un-

(6) R. A. Hoffman, S. Forsén, and B. Gestblom in "NMR, Basic Principles and Progress," Vol. 5, P. Diehl, E. Fluck, and R. Kosfeld, Ed., Springer-Verlag, New York, N. Y., 1971, p 41.

**Table I.** Comparison of the Observed Nmr Spectrum of *cis*-3,5-Dideuteriocyclopentene with That Calculated from the Parameters of Table II

Line no.	Obsd freq <sup>a</sup>	Calcd freq <sup>b</sup>	Calcd intensity <sup>b</sup>
1	171.40	171.37	0.171
2	173.00	172.99	0.186
3	174.60	174.60	0.007
4	178.60	178.66	0.226
5	179.40	179.38	0.236
6	180.25	180.24	0.250
7	180.25	180.30	0.250
8	185.60	185.57	0.006
9	187.05	187.03	0.319
10	187.05	187.07	0.329
11	199.50	199.50	0.019
12	214.95	214.95	0.006
13	216.30	216.27	0.017
14	220.90	220.89	0.347
15	221.80	221.86	0.324
16	228.00	227.98	0.248
17	228.70	228.71	0.234
18	229.15	229.15	0.233
19	229.30	229.30	0.233
20	235.50	235.54	0.188
21	237.00	236.95	0.174
22	c	241.74	0.005
23	c	242.18	0.002

<sup>a</sup> In Hz. <sup>b</sup> Normalized to 1 proton = 1. <sup>c</sup> Not observed.

**Table II.** Nmr Parameters for *cis*-3,5-Dideuteriocyclopentene

Chemical shifts, Hz <sup>a,b</sup>	Coupling constants, Hz <sup>b</sup>
$\nu_A = 228.16 \pm 0.01$	$J_{AB} = 5.63 \pm 0.04$
$\nu_B = 179.70 \pm 0.04$	$J_{AC} = 9.46 \pm 0.04$
$\nu_C = 180.82 \pm 0.04$	$J_{BC} = -12.74 \pm 0.02$

<sup>a</sup> At 100 MHz to low field of internal tetramethylsilane. <sup>b</sup> The errors are standard errors given by the computer program.

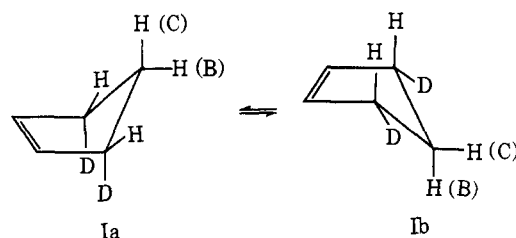
acceptable fit. The errors in  $\nu_B$  and  $\nu_C$  are therefore strongly correlated. The error matrix in the computer program also indicated a strong correlation between  $J_{AB}$  and  $J_{AC}$ , such that the sum of these coupling constants has a lower error than either of the individual coupling constants. After all errors are considered, the coupling constants given in Table II are unlikely to be in error by more than 0.1 Hz.

Isotope chemical shift effects resulting from substitution of a deuterium atom for a hydrogen atom in a CH<sub>2</sub> group are well established and always lead to an upfield shift of about 0.01 ppm.<sup>7</sup> The large chemical shift (0.057 ppm) difference between cyclohexane and cyclohexane-*d*<sub>11</sub> is presumably caused by  $\beta$  deuterons as well as by the  $\alpha$  deuteron.<sup>8</sup> In styrene- $\alpha$ -*d* the  $\beta$  hydrogens *cis* and *trans* to the deuterium are shifted by 0.006 and 0.003 ppm upfield, respectively.<sup>9</sup> In the present case, where the relative shift is 0.012 ppm, it is the proton *cis* to the deuteron which is shifted upfield with respect to the *trans* proton, on the assumption (see below) that the larger of the two vicinal coupling constants measured is between *cis* protons. A possible reason of the relatively large isotope shift in I is that the equilibrium constant for *Ia*  $\rightleftharpoons$  *Ib* differs very slightly from unity. If the chemical shift difference between H(B) and H(C)

(7) H. Batiz-Hernandez and R. A. Bernheim, *Progr. Nucl. Mag. Resonance Spectrosc.*, **3**, 63 (1967).

(8) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 86.

(9) E. I. Snyder, *J. Phys. Chem.*, **67**, 2873 (1963).



in *Ia* and *Ib* is 0.3 ppm, which is a plausible value, a  $K_{\text{equil}}$  of 0.96 is sufficient to account for the experimental results. Such an equilibrium constant corresponds to a  $\Delta G^\circ$  of only 24 cal/mol, a value even less than that observed in the equilibrium between the two conformations of 7-deuterio-1,3,5-cycloheptatriene<sup>10</sup> ( $\Delta G^\circ = 60$  to 70 cal/mol at  $-150^\circ$ ).

In accordance with the Karplus relationship, the vicinal coupling constants in nearly planar five-membered rings have the feature that  $J_{\text{cis}} \gg J_{\text{trans}}$  whereas when the ring is appreciably nonplanar the coupling constants are more nearly comparable.<sup>11</sup> In cyclopentene, the dihedral angle for the vicinal coupling constants under consideration is about  $23^\circ$ ,<sup>12</sup> and this should still make  $J_{\text{cis}} > J_{\text{trans}}$ . An accurate analysis of the proton spectrum of cyclopentene does not seem to have been carried out, although  $J_{\text{cis}}$  and  $J_{\text{trans}}$  have been reported to be 7.4 and 4.6 Hz, respectively.<sup>13</sup> These values must be only qualitatively correct, since we find that  $J_{\text{cis}}$  and  $J_{\text{trans}}$  for I are 9.5 and 5.6 Hz respectively, and isotope effects, even of the type discussed above, should not lead to differences greater than a few tenths of a hertz. In the ethylene ketal of cyclopentenone,  $J_{\text{cis}}$  and  $J_{\text{trans}}$  are 8.6 and 4.2 Hz, respectively,<sup>14</sup> and the lower values as compared to I are presumably due to the electronegativity of the substituents. In all these compounds, the coupling constants are, of course, averages involving two equally populated nonplanar conformations analogous to *Ia* and *Ib*. A comparison can also be made with *cis*-3,5-dibromocyclopentene, where  $J_{\text{cis}}$  and  $J_{\text{trans}}$  are 6.9 and 1.5 Hz, respectively,<sup>15</sup> but here the average is between two unequally populated conformations, and substituent effects are probably substantial.

In view of the anomalies in the vicinal coupling constants in five-membered rings,<sup>16</sup> it is important to have reliable values for the coupling constants in key reference compounds, such as cyclopentene. The values found in the present work are appreciably higher than those predicted<sup>16</sup> on the basis of a Karplus relationship ( $J_{\text{cis}} = 8.9$  Hz,  $J_{\text{trans}} = 3.1$  Hz), especially for  $J_{\text{trans}}$ .

The nmr spectrum of the reaction product of cyclopentadiene and deuterium is consistent with the presence of I and the lines in the spectrum which do not belong to I can be recognized as belonging to cyclopentene itself

(10) F. R. Jensen and L. A. Smith, *J. Amer. Chem. Soc.*, **86**, 956 (1964).

(11) F. A. L. Anet and R. Anet in "Determination of Organic Structures by Physical Methods," Vol. 3, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., 1971, Chapter 7.

(12) (a) G. W. Ratjens, Jr., *J. Chem. Phys.*, **36**, 2401 (1962); (b) J. Laane and R. C. Lord, *ibid.*, **47**, 4941 (1967).

(13) R. J. Abraham, "NMR for Organic Chemists," D. W. Mathieson, Ed., Academic Press, New York, N. Y., 1967, p 142.

(14) C. H. Depuy, C. E. Lyons, and C. B. Rodewald, *J. Chem. Eng. Data*, **11**, 102 (1966).

(15) H. J. Jakobsen, *Tetrahedron Lett.*, 1991 (1967).

(16) R. J. Abraham, K. Parry, and W. A. Thomas, *J. Chem. Soc. B*, 446 (1971).

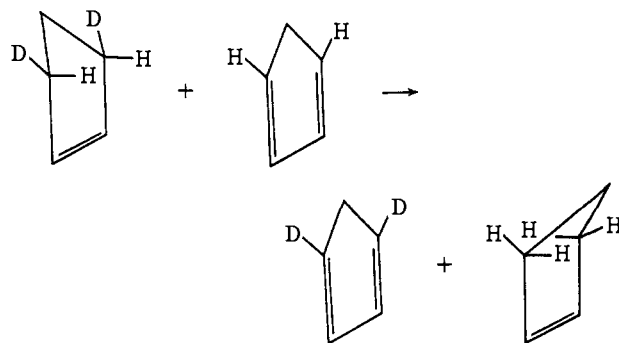
in the following way. The bands marked with an asterisk in Figure 1 were unchanged when the deuterium decoupling frequency was removed. Thus these bands *cannot* correspond to a deuterated species. Furthermore, the allylic methylene region of the nmr spectrum of cyclopentene, measured under the same conditions as those used for the spectrum of Figure 1 (except that no deuterium decoupling was employed), gave bands which corresponded exactly in frequency and fine structure with the asterisked band on the left-hand side in Figure 1.

The chemical shift of the allylic CHD protons in I is at a distinctly higher field than that of the allylic protons in cyclopentene, owing to the isotope effect resulting from deuterium substitution on a CH<sub>2</sub> group.<sup>7</sup> The nonallylic (upfield) methylene protons in cyclopentene are a rough 1:4:6:4:1 quintet with additional fine structure. In Figure 1 only the outer components, in which the fine structure results in doublets, are marked with asterisks. The inner components of the quintet are partly under and partly on the sides of the strong lines of the methylene band of I.

The question now arises as to whether the spectrum assumed to belong to I cannot possibly be fitted to other species of deuterated cyclopentene. Any 1,2-addition product requires an allylic to homoallylic proton ratio of 3:1 instead of the 1:1 required by the observed spectrum, and additionally would not give rise to a spectrum of the A<sub>2</sub>BC type. Although the presence of a few per cent or less of 1,2-addition product cannot be ruled out, the reaction is certainly predominantly 1,4 at a reaction temperature of 300°. The contrast between our results and those of Baldwin<sup>4c</sup> can be explained by the much higher temperature, namely, 550°, used by the latter author. It appears therefore that 1,2-addition or elimination processes have higher activation energies than the corresponding 1,4 processes in the present system.

Finally, the 1,4-addition product must have the deuterons *cis* to one another, since the *trans* adduct would lead to an AA'BB' spectrum, which is not in agreement with that observed because an AA'BB' spectrum is symmetrical about its center frequency. Thus, the uncatalyzed addition of molecular hydrogen to cyclopentadiene takes place most easily by a concerted reaction and is in accordance with the Woodward-Hoffmann rules.<sup>5</sup> Since cyclopentadiene is an extremely reactive olefin in the Diels-Alder reaction, it is unlikely that the uncatalyzed addition of H<sub>2</sub> to less reactive conjugated dienes can be observed. The reverse reaction, *i.e.*, elimination of H<sub>2</sub>, is of course, easier to observe, especially when an aromatic ring is created.<sup>3</sup>

The most likely explanation for the undeuterated cyclopentene is the existence of a concerted suprafacial double-group transfer of two hydrogen atoms from *cis*-3,5-dideuteriocyclopentene to cyclopentadiene as shown below. Such a reaction is allowed by the Woodward-



Hoffmann rules<sup>5</sup> and this kind of reaction is known in other systems.<sup>17</sup> The analogous transfer of two deuteriums results in no net change and is therefore an invisible reaction in the present system.

### Experimental Section

***cis*-3,5-Dideuteriocyclopentene.** Cyclopentadiene (2.3 g) and phenothiazine (0.5 g) were placed in a 250-ml stainless-steel hydrogenation vessel. After removal of the air, deuterium gas was introduced until the pressure reached about 35 atm, and then the vessel was shaken and heated to 300–310° for 4.5 hr. After being cooled to room temperature, the contents of the vessel were collected in a liquid nitrogen-cooled trap, and the last traces of volatile matter were transferred by applying a vacuum for 30 min. The volatile matter in the trap amounted to 0.25 g while much rubbery resinous matter remained in the hydrogenation vessel. Analysis of the volatile portion by vpc on a 5-ft column of 1,2,3-tris(2-cyanoethoxy)propane at 25° (helium flow rate of 30 ml/min) revealed two components in the ratio of 2:1 with retention times of 7 and 13 min, corresponding to cyclopentene and cyclopentadiene, respectively. Cyclopentane, which has a retention time of 4 min under the above conditions, was not present.

**Instrumentation.** For nmr examination, the cyclopentene fraction was made into about a 4% solution in deuteriochloroform containing a small amount of TMS as a lock signal and a trace of acetone as a reference line for measuring the resolution. Spectra were measured on a Varian HA100 spectrometer equipped with a deuterium decoupler made by NMR Specialties, Inc. The spectra were obtained on 100-Hz sweep widths and the frequency was calibrated every 10 Hz with a frequency counter. Calculations of spectra were carried out with the LAOCOON III program of Bothner-By and Castellano.<sup>18</sup>

(17) W. v. E. Doering and J. W. Rosenthal, *J. Amer. Chem. Soc.*, **89**, 4535 (1967); P. Dowd and I. Fleming, unpublished work quoted in ref 5.

(18) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).