

of cyclooctane, 1-octene, and 2,3-di-*t*-butyl-1,3-butadiene. The data were treated in the manner described above and three or more runs with different initial ratios of 1-octene to diene were made in each case.

**Inhibitory Effect of 2,3-Di-*t*-butyl-1,3-butadiene.**—A solution consisting of 20 mole % 1-octene in bromotrichloromethane was illuminated at 56° with a 275-w sunlamp. Samples of the reaction mixture were withdrawn at 3-min intervals and the amount of 1-octene was determined by gas chromatographic analysis. Within 15 min, the 1-octene was completely consumed. A similar mixture containing 10 mole % 2,3-di-*t*-butyl-1,3-butadiene was subjected to the same treatment. During the first 15 min, very little of the 1-octene was consumed. After 80 min of illumination, approximately 50% of the 1-octene had undergone reaction with the bromotrichloromethane.

Following the rate of reaction of 1-octene (15 mole %) with *n*-butyl mercaptan in light-induced reactions at 56° by de-

termining the 1-octene remaining in samples withdrawn from the reaction mixture at 3–5-min intervals showed that the presence of I (15 mole %) has no appreciable effect on the rate of reaction of the alkene with the mercaptan. In both cases, the half-life of the 1-octene was about 8–10 min.

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## Cycloadditions. IX. Mechanism of the Thermal Interconversion of *exo*- and *endo*-Dicyclopentadiene<sup>1</sup>

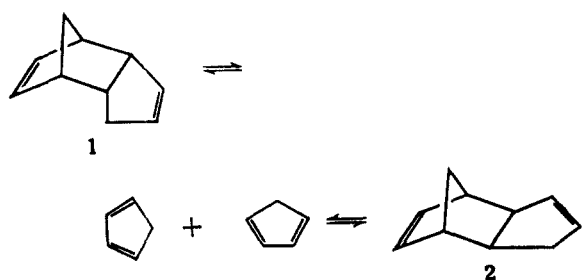
JOHN E. BALDWIN

*Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801*

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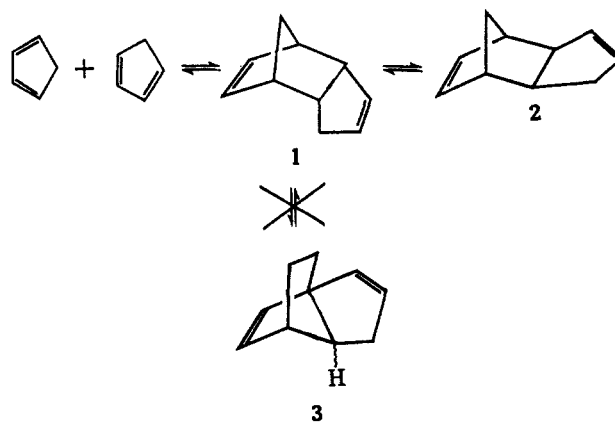
At 196°, *endo*-dicyclopentadiene specifically labeled with deuterium in one cyclopentadiene moiety rearranges by way of kinetically free cyclopentadiene to give *exo*-dicyclopentadiene having a scrambled deuterium distribution. Labeled *endo*-dicyclopentadiene recovered after short reaction times is only partially scrambled, while *exo*-dicyclopentadiene maintains its labeling integrity under the reaction conditions.

The thermal isomerization of *endo*-dicyclopentadiene (1) to *exo*-dicyclopentadiene (2) was observed and rationalized mechanistically by Alder and Stein in 1933.<sup>2</sup> They held<sup>2</sup> that at 170° an equilibrium between the *endo* dimer and cyclopentadiene affords a significant concentration of the monomer, and that redimerization of the cyclopentadiene could give either isomeric dicyclopentadiene.



At 180–240°, *endo*-dicyclopentadiene was converted to an isomer initially proposed<sup>3</sup> to be a tricyclo-[4.2.2.0<sup>1,5</sup>]deca-2,7-diene (3) but soon recognized<sup>4</sup> as the *exo* dimer 2. This isomer (2) was found<sup>3</sup> to be unable to dissociate at these temperatures directly to two molecules of cyclopentadiene. It was transformed intramolecularly to *endo*-dicyclopentadiene with an activation energy of 8 kcal/mole, and the *endo*-diene in turn suffered cycloelimination to give a monomer.<sup>3</sup>

The rationale of Alder and Stein and the reports of Schröder are incompatible; this disparity seemed to



call for fresh experimentation. An internal pathway for the interconversion of *endo*- and *exo*-dicyclopentadiene would constitute a rare example of an intramolecular *endo*-*exo* isomerization of a Diels-Alder adduct that might have far-reaching mechanistic significance.<sup>5</sup>

**Experimental Design.**—An experimental distinction between intramolecular and intermolecular mechanistic pathways for the interconversions of *endo*- and *exo*-dicyclopentadiene was sought through a study of the rearrangements of dienes appropriately labeled with deuterium.

The distinction depends, in principle, on the different predictions one would make for the thermal rearrangement of a dicyclopentadiene labeled with deuterium in only one ring. If neither isomer dissociated reversibly to cyclopentadiene during the rearrangement, an internal pathway for the interconversion would give the isomeric diene containing the same deuterium

(1) This work has been supported by the National Science Foundation (Grant No. GP-5226) and by a Du Pont Grant-in-Aid to the Department of Chemistry and Chemical Engineering of the University of Illinois. Paper VII in this series: I. C. Paul, J. E. Baldwin, and R. A. Smith, *J. Am. Chem. Soc.*, in press. Paper VIII: J. E. Baldwin, J. A. Kapecki, M. G. Newton, and I. C. Paul, *Chem. Commun.* (London), in press.

(2) K. Alder and G. Stein, *Ann.*, **504**, 216 (1933).

(3) W. Schröder, *Angew. Chem.*, **72**, 865 (1960).

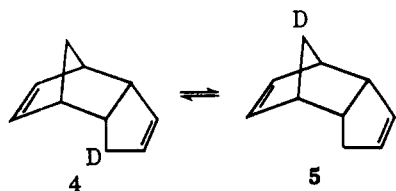
(4) W. Schröder, *ibid.*, **73**, 241 (1961).

(5) C. Ganter, U. Scheidegger, and J. D. Roberts [*J. Am. Chem. Soc.*, **87**, 2771 (1965)] have given a rigorous test for an internal pathway in another *exo*-*endo* isomerization, and a summary of the pertinent literature.

content as the starting material, while an external pathway, involving intermediate formation of cyclopentadiene, would give rise to a scrambled deuterium distribution in the product. If kinetic isotope effects may be ignored, the scrambled distribution may be calculated. For instance, specifically labeled *endo*-diene (100%  $d_1$ ) would rearrange by way of cyclopentadiene (50%  $d_0$ , 50%  $d_1$ ) to give *exo*-diene (25%  $d_0$ , 50%  $d_1$ , 25%  $d_2$ ). Since the  $d_1$  dimer could be formed in two ways, the rate constant for dimerization of a  $d_0$ - and a  $d_1$ -cyclopentadiene would be larger than the rate constant for dimerization of two  $d_0$ -cyclopentadienes or two  $d_1$ -cyclopentadienes by a factor of 2.

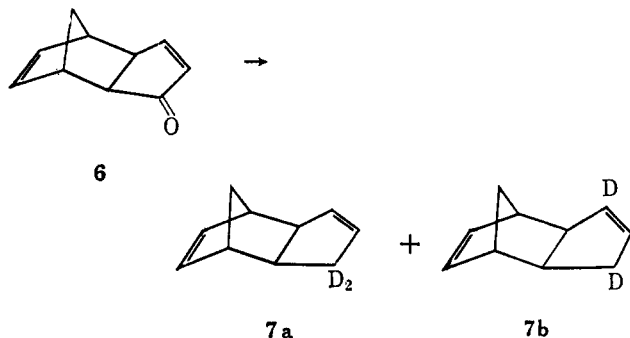
This simple picture is complicated by possible reversible dissociation of one or both dienes under the reaction conditions. A specifically labeled diene, which dissociates to two molecules of cyclopentadiene and is then reformed, has its deuterium label scrambled in the process. Thus, rearrangement of one specifically labeled dicyclopentadiene to the other isomer with retention of labeling specificity would have immediate mechanistic significance and would give strong support to an internal pathway, but rearrangement giving a scrambled isotopic composition in the isomeric diene could be taken as evidence for the external mechanism only if it would be shown that the isomeric product was stable under the reaction conditions and that the starting diene had not equilibrated its label prior to rearrangement.

It will be noted that *endo*-diene labeled specifically in only one ring may be converted intramolecularly through a Cope or Woodward-Katz<sup>6</sup> rearrangement to a diene having label in the other cyclopentadiene moiety (e.g., **4**  $\rightleftharpoons$  **5**). This likely process does not obscure the test for internal or external pathways for interconversion of *exo* and *endo* isomers: either **4** or **5**, or both **4** and **5** would serve equally well as a specifically labeled substrate.



### Results and Discussion

Syntheses of the required specifically labeled dienes were accomplished with metal hydride reductions. *exo*-Dicyclopentadien-1-one (**6**) was reduced with



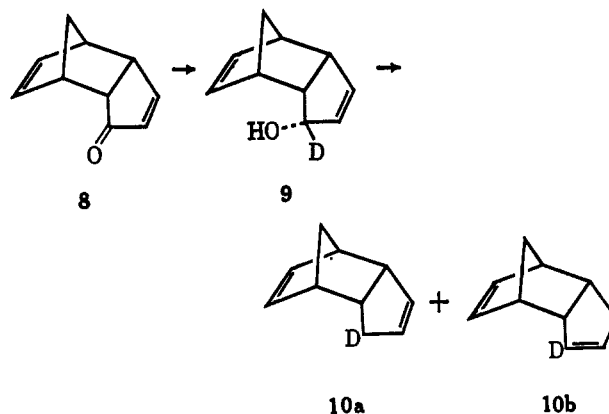
(6) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

TABLE I  
DEUTERIUM DISTRIBUTIONS IN DICYCLOPENTADIENES ON  
*exo* TO *endo* REARRANGEMENT AT 196°

Time, min	Rearrangement %	<i>endo</i> -Diene 1					<i>exo</i> -Diene 2	
		$d_0$	$d_1$	$d_2$	$d_3$	$d_4$	$d_1$	$d_2$
0	0						8	92
90	20	51	5	38	1	5	9	91

"dichloroaluminum deuteride"<sup>7</sup> to give *exo*-dicyclopentadiene (**7**) which was shown by mass spectrometry to be 8%  $d_1$  and 92%  $d_2$ . That the labeled *exo*-diene is probably a mixture of **7a** and **7b** does not complicate the situation, for the important specificity has been achieved: the label, in this instance two deuterium atoms, has been introduced in one cyclopentadiene unit of the dimer.

While this synthetic approach gave cleanly labeled product, the yield was low. To secure the larger quantities of labeled *endo*-diene required, *endo*-dicyclopentadien-1-one (**8**) was reduced with lithium aluminum deuteride to give 1-deuterio- $\beta$ -1-hydroxy-*endo*-dicyclopentadiene (**9**). This allylic alcohol was reduced with "dichloroaluminum hydride" to give *endo*-dicyclopentadiene (**10**) having the isotopic composition 6%  $d_0$ , 80%  $d_1$ , 4%  $d_2$ , and 10%  $d_3$ .



The specifically labeled *exo*-dicyclopentadiene (**7**) was purified for the rearrangement by preparative glpc on a  $\beta, \beta'$ -oxydipropionitrile column, under conditions where complete separation of *exo* and *endo* isomers was achieved. It was heated as a solution in cyclohexane at 196° for 90 min; both isomers were collected by preparative glpc and analyzed by mass spectrometry. The results obtained for the thermal conversion of labeled *exo*-dicyclopentadiene to the *endo*-diene are summarized in Table I.

The *exo*-dideuteriodicyclopentadiene is isotopically stable to the reaction conditions, while the rearrangement product is a mixture of several isotopic species. This mixture is in quantitative accord with none of the three principal results projected as formal possibilities. Internal isomerization without subsequent scrambling *via* cyclopentadiene would have given the *endo* isomer with 8%  $d_1$  and 92%  $d_2$ . Internal isomerization followed by complete scrambling or an exclusively external rearrangement pathway would have given an isotopic distribution in the *endo*-diene of 25%  $d_0$ , 4%  $d_1$ , 46%  $d_2$ , 4%  $d_3$ , and 21%  $d_4$ . Finally, an internal isomerization with subsequent incomplete scrambling of label by way of cyclopentadiene would have given a composi-

(7) J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 116 (1964), and references cited therein.

tion expressible as a linear combination of the first two possibilities. The significance of this result is considered below.

Samples of the specifically labeled *endo*-deuteriodicyclopentadiene (**10**) were heated at 196° for 7, 60, and 90 min. Both starting material and the *exo*-diene formed were isolated from each sample by glpc and analyzed by mass spectrometry (Table II).

TABLE II

DEUTERIUM DISTRIBUTIONS IN DICYCLOPENTADIENES ON *endo* TO *exo* REARRANGEMENT AT 196°

Time, min	Rearrangement, %	<i>endo</i> -Diene 1				<i>exo</i> -Diene 2			
		<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>
0	0	6	80	4	10				
7	1.1	25	60	13	2				
7	1.1	26	57	16	1	30	47	19	4
60	11	34	42	18	5	28	49	22	2
90	16	67	20	9	3	31	47	21	1

The theoretical values for the deuterium distribution to be expected from a completely scrambled diene derived from the partially labeled starting material (**10**) depend on the assumptions one makes. If the *d*<sub>3</sub> component in **10** stems from molecules having all three deuteriums in one cyclopentadiene unit, a scrambled product would be 28.1% *d*<sub>0</sub>, 42.4% *d*<sub>1</sub>, 18.1% *d*<sub>2</sub>, 6.9% *d*<sub>3</sub>, 4.0% *d*<sub>4</sub>, 0.2% *d*<sub>5</sub>, and 0.3% *d*<sub>6</sub>. The agreement between the theoretical values for totally scrambled diene and the experimental values for the *exo*-dicyclopentadiene in Table II is improved when both are put on the same basis (when the sum of percentages of *d*<sub>0</sub>, *d*<sub>1</sub>, *d*<sub>2</sub>, and *d*<sub>3</sub> species is taken as 100%). With this normalization correction, the theoretical values become 29.4% *d*<sub>0</sub>, 44.4% *d*<sub>1</sub>, 19% *d*<sub>2</sub>, and 7% *d*<sub>3</sub>. The agreement is within estimated experimental error; the product from the thermal rearrangement, the *exo*-diene, is completely scrambled. At short reaction times (1% rearrangement) the starting material, the deuterium-labeled *endo*-dicyclopentadiene, is only partially scrambled. Hence, an external mechanism, in which the thermal interconversion of *endo*- and *exo*-dicyclopentadiene proceeds principally or exclusively through a cycloelimination, cycloaddition sequence involving intermediate formation of kinetically free cyclopentadiene is indicated.

From the percentages of *d*<sub>1</sub> and *d*<sub>2</sub> species present in the recovered *endo*-dicyclopentadiene after 7 min at 196°, one can estimate that the label of the starting diene has been about 60% scrambled. The experimental value for the *d*<sub>0</sub> contribution, 25–26%, is somewhat larger than might have been expected for 60% scrambling (20%). This discrepancy may be an early manifestation of the enhanced *d*<sub>0</sub> contribution that becomes prominent at longer reaction times. The estimate of 60% scrambling is in reasonably good agreement with expectations based on other work. The rate constant for dissociation of dicyclopentadiene in the gas phase at 196° is about  $1.5 \times 10^{-3} \text{ sec}^{-1}$ ,<sup>8</sup> a reaction proceeding at this rate for 7 min would go to 50% completion.<sup>9</sup>

(8) J. B. Harkness, G. B. Kistiakowsky, and W. H. Mears, *J. Chem. Phys.*, **5**, 682 (1937).

(9) S. G. Smith and I. D. R. Stevens, *J. Chem. Ed.*, **38**, 574 (1961).

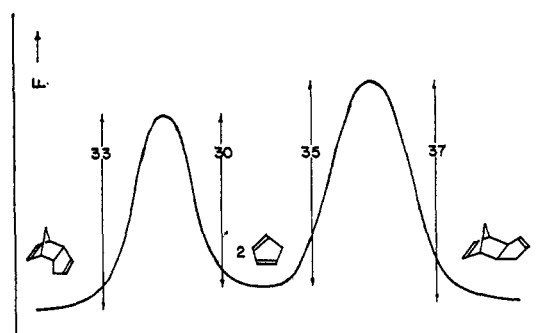


Figure 1.—Reaction profile for the interconversion of *exo*- and *endo*-dicyclopentadiene at 196°. The estimated free energies of activation are given in kcal mole<sup>-1</sup>.

How large a proportion of the rearrangement of *endo*- to *exo*-dicyclopentadiene (Table II) may have gone by an internal pathway, competitive with the external cycloelimination–cycloaddition route? The fact that the deuterium distributions in the *exo*-diene formed during the rearrangement remain constant within experimental error from 1 to 16% rearrangement, while the *endo*-diene changes from an unscrambled to a partially scrambled to a completely scrambled condition, suggests that an internal pathway must be of negligible importance.

An internal rearrangement from the *endo*-diene during the first 7 min of the reaction would have given *exo*-diene having an isotopic composition of 13% *d*<sub>0</sub>, 69% *d*<sub>1</sub>, and 8% *d*<sub>2</sub>.<sup>10</sup> If  $\pm 3\%$  is taken as an accurate estimate of experimental error in determining the isotopic composition of the *exo*-dicyclopentadiene produced, then the experimental results require that less than one-sixth of the rearranged diene could have been formed by an internal mechanism. The results are consistent with an exclusively external pathway for interconversion, but the experimental error associated with the method and labeled compounds used still leaves room for a minor contribution from an internal rearrangement.

The deuterium compositions of the *endo*-diene after 90 min at 196° (Tables I and II) seem to indicate that some deuterium has been lost. A radical mediated exchange between cyclopentadiene and cyclohexane may be involved.

## Conclusions

Using the data of Tables I and II, data available from the literature,<sup>11,12</sup> and needed approximations, one can construct the reaction profile for the interconversion of *endo* and *exo*-dicyclopentadiene shown in Figure 1. It provides a semiquantitative restatement in visual terms of the mechanism proposed by Alder and Stein<sup>2</sup> and reaffirmed in the present work (Figure 1).

The results of this investigation are fully compatible with the interconversion of the two isomeric Diels–Alder adducts **1** and **2** through a dissociation, recombination sequence in which the cyclopentadiene molecules produced as intermediates are free to switch partners before they redimerize.

(10) The calculations leading to these estimates are analogous to those described in detail in ref 5.

(11) H. Kaufmann and A. Wassermann, *J. Chem. Soc.*, 870 (1939).

(12) A. Wassermann, *Monatsh.*, **83**, 543 (1952).

### Experimental Section<sup>13</sup>

**exo-Dicyclopentadiene** was prepared by the procedure of Bartlett and Goldstein<sup>14</sup> and had bp 55–60° (9–12 mm). Analysis of the product by glpc showed that it contained some *endo* isomer.<sup>15</sup>

**exo-Dicyclopentadien-1-ol**.—Oxidation of 16.1 g (0.122 mole) of *exo*-dicyclopentadiene with 6.65 g (0.06 mole) of selenium dioxide in wet dioxane, according to the procedure given by Woodward and Katz<sup>6</sup> for a similar oxidation, gave 4.99 g (28% yield) of product, bp 85–86° (1 mm). Redistillation gave a sample having  $n_D^{25}$  1.5294.

Careful redistillation through a 10-cm glass helix packed column gave material of bp 98–100° (4 mm),  $n_D^{20}$  1.5311. A sample of this distillate, purified by preparative glpc on an XF 1150 column at 143°, evidently was still not completely pure, because its carbon analysis was 1.88% low.<sup>16</sup>

The phenylurethane was prepared and after recrystallization from methylcyclohexane it had mp 133–134° (lit. mp 130–132°,<sup>17</sup> 127°<sup>18</sup>).

*Anal.* Calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>: C, 76.38; H, 6.41. Found: C, 76.23; H, 6.41.

The 3,5-dinitrobenzoate derivative, obtained in 83% yield from the distilled alcohol, had mp 139–141° dec after recrystallization from ethanol–water–acetonitrile.

*Anal.* Calcd for C<sub>17</sub>H<sub>17</sub>N<sub>2</sub>O<sub>6</sub>: C, 59.65; H, 4.12. Found: C, 59.45; H, 4.19.

**exo-Dicyclopentadien-1-one**.—Oxidation of 6.9 g (0.047 mole) of *exo*-dicyclopentadien-1-ol with Jones reagent according to a general procedure<sup>19</sup> gave a reaction mixture that was worked up by decanting the acetone solution of product from precipitated salts, removing the acetone by rotary evaporation, and dissolving the residue in 100 ml of ether. The ethereal solution was washed with aqueous sodium bicarbonate, dried over calcium sulfate, filtered, concentrated, and distilled. Distillation gave 5.6 g (82% yield) of *exo*-dicyclopentadien-1-one, bp 86–91° (2 mm) [lit.<sup>18</sup> bp 82° (0.5 mm)]. A sample further purified by preparative glpc on an XF 1150 column was not analytically pure.

**exo-Dideuteriodicyclopentadiene**.—Ethereal "dichloroaluminum deuteride"<sup>20</sup> was prepared from 10.5 g (0.079 mole) of aluminum chloride, 1.1 g (0.026 mole) of lithium aluminum deuteride (Metal Hydrides Incorporated, 97%), and 200 ml of ether. To this solution in a 500-ml three-necked flask was added with stirring under an argon atmosphere a solution of 2.95 g

(0.02 mole) of *exo*-dicyclopentadien-1-one in 8 ml of ether. The addition was completed in 15 min. The reaction mixture was stirred at room temperature for another 3.8 hr, then poured into ice–water, made acidic with dilute hydrochloric acid, and washed with water and with saturated aqueous sodium chloride. The ethereal solution was dried over calcium sulfate, filtered, and concentrated by distillation. Flash distillation gave 0.27 g (10%) of product, bp 50° (8 mm), shown by glpc analysis to be a mixture of *exo*- and *endo*-dicyclopentadiene. The *exo* isomer was isolated by preparative glpc. That the material so purified was free from contamination by the *endo*-diene was established by chromatography. The purified *exo*-diene for the thermal rearrangement experiment was 8% *d*<sub>1</sub> and 92% *d*<sub>2</sub>.

**endo-Deuteriodicyclopentadiene**.—A solution of 4 g (0.027 mole) of *endo*-dicyclopentadien-1-one<sup>6,20</sup> in 40 ml of ether was added in 7 min at room temperature to a stirred solution of 0.5 g (0.012 mole) of lithium aluminum deuteride in 200 ml of ether under an argon atmosphere. The reaction mixture was stirred at room temperature for 1 hr, refluxed for 5 min, cooled in an ice bath, and hydrolyzed by the successive addition of 0.2 ml of water, 0.2 ml of 15% sodium hydroxide, and 0.6 ml of water.<sup>21</sup> Filtration of the hydrolyzed reaction mixture and concentration of the filtrate under reduced pressure gave 4.0 g of a colorless crystalline material. A solution of this unpurified product in 40 ml of ether was added to a stirred solution of 40 ml of 3*N* "dichloroaluminum hydride"<sup>22</sup> in 3 min at room temperature. After an additional 40 min at room temperature, 15 min at reflux, and 30 min at room temperature, the reaction mixture was poured into ice–water. The resulting mixture was acidified with dilute hydrochloric acid and washed with water and with saturated aqueous sodium chloride; the ethereal solution was dried over calcium sulfate, filtered, and concentrated by distillation. Vacuum distillation of the residue on a 20-cm spinning-band column gave 1.2 g (33% yield) of *endo*-deuteriodicyclopentadiene, bp 53–58° (15 mm). Analysis of the product by glpc showed the complete absence of *exo*-diene. The mass spectrum of the product revealed an isotopic composition of 6% *d*<sub>0</sub>, 80% *d*<sub>1</sub>, 4% *d*<sub>2</sub>, and 10% *d*<sub>3</sub>.

**Thermal Rearrangements of Deuterium-Labeled Dicyclopentadienes**.—A solution of *exo*-dideuteriodicyclopentadiene (79 mg) and 145 mg of cyclohexane was sealed in a Pyrex tube and heated in refluxing decalin (196°) for 90 min. The tube was cooled and opened; samples of both the rearrangement product, *endo*-dicyclopentadiene, and recovered starting material were collected by preparative glpc and analyzed by mass spectrometry. The results are summarized in Table I.

*endo*-Deuteriodicyclopentadiene (622 mg), cyclohexane (530 mg), and hydroquinone (12 mg) were sealed in a Pyrex tube and heated in refluxing decalin (196°) for 7 min. The tube was quenched in ice–water and the samples of the rearrangement product, *exo*-dicyclopentadiene, and recovered starting material were isolated by glpc and submitted for mass spectrometric analyses. Similar experiments were performed with ampoules containing aliquots of a solution of *endo*-deuteriodicyclopentadiene (376 mg) and cyclohexane (565 mg) and added hydroquinone. These ampoules were heated at 196° for 60 or 90 min and processed as described above. The mass spectrometric results are summarized in Table II.

(20) K. Alder and F. H. Flock, *Chem. Ber.*, **87**, 1916 (1954).

(21) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(13) Analyses are by J. Nemeth and associates, Urbana, Ill. Melting points and boiling points are uncorrected. Mass spectra were determined by J. Wrona with an Atlas CH-4 instrument, using low electron energies (<13 eV) and wide slits. Separations of *exo*- and *endo*-dicyclopentadiene were accomplished on a 9 mm × 2.5 m column of β,β'-oxydipropionitrile (21% on nonacid-washed 60–80 mesh Chromosorb P) at 65°, using either a Wilkins Model A-90-P or an F & M Model 300.

(14) P. D. Bartlett and I. S. Goldstein, *J. Am. Chem. Soc.*, **69**, 2553 (1947); see also A. A. Oswald and F. Noel, *J. Org. Chem.*, **26**, 3948 (1961).

(15) Compare H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964).

(16) This alcohol has been made by two groups of workers,<sup>17,18</sup> but neither has reported elemental analyses for the compound.

(17) K. Alder, F. H. Flock, and P. Janssen, *Chem. Ber.*, **89**, 2689 (1956).

(18) R. C. Cookson, N. S. Isaacs, and M. Szelke, *Tetrahedron*, **20**, 717 (1964).

(19) C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).