

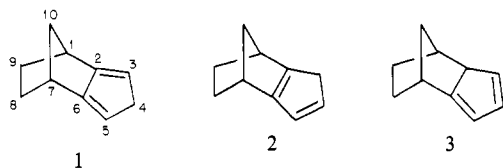
Tracer Studies of the 1,5 Sigmatropic Hydrogen Shifts in Isodicyclopentadiene

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Abstract: By way of the lithium derivative of isodicyclopentadiene **1**, a single deuterium atom can be introduced at -78°C into the ring largely at position $4\alpha(\text{endo})$, with lesser amounts at $4\beta(\text{exo})$ and at 3 and 5. Positions of the deuterium can be determined by ^1H , ^2H , and ^{13}C NMR spectroscopy on the dienes and on their adducts with dimethyl acetylenedicarboxylate (DMAD) and maleic anhydride, and lanthanide-induced shifts in the ^1H spectra of these adducts. At all temperatures, and conveniently at 100°C , the deuterium is redistributed in a thermal, noncatalytic reaction to yield equal amounts of deuterium at positions 3, 4α , 4β , and 5. Despite the obvious role of rearranged cyclopentadiene structures such as **2** and **3** in these shifts, no diene structures other than that of **1** can be detected in the isolated samples under these conditions. A kinetic study of these shifts allows assignment of rate constants to the elementary processes and indicates an isotope effect $k_{\text{H}}/k_{\text{D}} = 6.5$. At 0°C in ether or tetrahydrofuran, the use of D_2O with lithium isodicyclopentadienide leads to as much as 62% of the previously undetected isomer **3**, deuterated at the ring junction (structure **5**, Table III). This species, which has been isolated and characterized, is less reactive than **1** toward maleic anhydride.

It was observed recently¹ that the reversible 1,5 sigmatropic hydrogen shifts in the system **1** \rightleftharpoons **2** of isodicyclopentadiene control



the course of diene additions in ways that depend on the dienophile: vinylene carbonate adds only to **2**, under conditions of rapid equilibration (180°C), dimethyl acetylenedicarboxylate (DMAD) adds only to **1** under any conditions, and maleic anhydride is reactive toward both isomers. The sigmatropic shift conforms to the indene model² in being noncatalytic and also in proceeding to such an unfavorable equilibrium that the second isomer is detected only by trapping. The third possible diene structure **3** of isodicyclopentadiene did not appear to participate in these diene competitions.

In this paper we describe a detailed study of the sigmatropic shifts in deuterium-labeled isodicyclopentadiene, including rate measurements and a kinetic analysis of the elementary process.

Results

Treatment of isodicyclopentadiene **1** with dimethylsodium or with dimyllithium (1:1) in $\text{Me}_2\text{SO}-d_6$ leads to a product whose NMR spectra show none of the peaks of **1**, but the characteristic anion spectra listed in Tables I and II. The delocalization in the anion is reflected in a downfield shift of 57 ppm at C-4 with an accompanying $^1J_{\text{CH}}$ of 151 Hz. The other four carbon atoms of the cyclopentadienide ion system show *upfield* shifts relative to **1** in the ^{13}C NMR spectrum, consistent with the delocalization of an electronic charge around the ring in the anion.

Assignments of the proton NMR peaks shown in Table II are based on spin decoupling, coupling constants, and integrated intensities. The three protons at positions 3, 4, and 5 in the anion have similar chemical shifts.

Deuterium Labeling of 1. For the purpose of introducing a single deuterium atom into **1** it proved advantageous to operate at -78°C with tetrahydrofuran as solvent, to avoid the heterogeneity of Me_2SO solutions at that temperature. Under these conditions

Table I. ^{13}C Data of IDCP and Its Anion^a

	δ ($\text{Me}_2\text{SO}-d_6$)	$^1J_{\text{CH}}$, Hz	δ (Me_4Si) ($\text{Me}_2\text{SO}-d_6$)	δ (Me_4Si) (CDCl_3)	$\Delta\delta^b$
C-2, C-6	127.8		127.5	155.8	-28.0
C-4	102.4	151	102.1	45.2	57.2
C-3, C-5	93.0	142	93.2	114.0	-11.0
C-10	51.0	134	51.2	48.2	4.8
C-1, C-7	41.1	146	40.9	38.5	2.6
C-8, C-9	30.8	130	30.8	28.6	2.2

^a $\delta_{\text{Me}_4\text{Si}} = 0$. ^b $\Delta\delta = \delta_{\text{dienide}} - \delta_{\text{diene}}$.

Table II. Proton Chemical Shifts in Sodium and Lithium Isodicyclopentadienides (in $\text{Me}_2\text{SO}-d_6$)^a

	i	ii
H-4	δ 5.06, $J_{3-4} = 2.7$ Hz	δ 4.94, $J_{3-4} = 2.6$ Hz
H-3, H-5	δ 4.98	δ 4.89
H-1, H-7	δ 2.93	δ 2.90
H-8 β , H-9 β	δ 1.58, $J_{8\alpha-9\beta} = 5.0$ Hz	δ 1.57
H-10 α	δ 1.46, $J_{10\alpha-10\beta} = 6.8$ Hz	δ 1.48
H-10 β	δ 1.32, $J_{9\alpha-10\beta} = 1.0$ Hz	δ 1.30
H-8 α , H-9 α	δ 0.68	δ 0.68

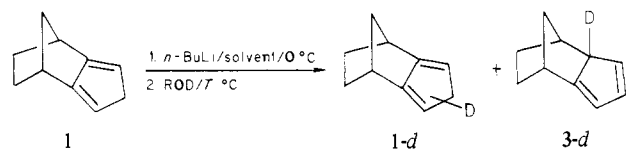
^a $\delta_{\text{Me}_4\text{Si}} = 0$.

lithium isodicyclopentadienide (prepared via *n*-butyllithium in THF) reacted with either CH_3OD or $(\text{CH}_3)_3\text{COD}$ to yield a monodeuterated diene which could be purified by extraction and distillation below room temperature, examined by NMR, and converted into diene adducts with maleic anhydride and DMAD. The extent of deuteration, as determined by the integrated intensities of H-3, H-4, and H-5 in the ^1H NMR spectra compared with an internal standard, was 1.00-1.05. The deuterium in a typical sample was mainly at $4\alpha(\text{endo})$ (79.5%) with 17% at $4\beta(\text{exo})$ and 3.5% at the equivalent 3 and 5 positions. The NMR signal of H-3,5 is distinguishable from that of H-4, but to

(1) Subramanyam, R.; Bartlett, P. D.; Iglesias, G. Y. M.; Watson, W. H.; Galloy, J. J. *Org. Chem.* **1982**, *47*, 4491.

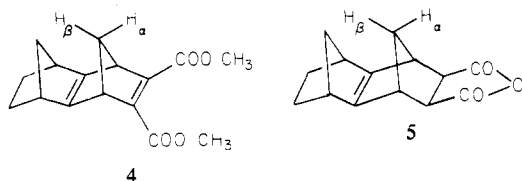
(2) (a) Alder, K.; Pascher, F.; Fagt, H. *Chem. Ber.* **1942**, *75*, 1501. (b) Berson, J. A.; Aspelin, G. B. *Tetrahedron* **1964**, *20*, 2697. (c) Roth, W. R.; *Tetrahedron Lett.* **1964**, 1009.

Table III



solvent	ROD	T, °C	product composition, mole %	
			1-d	3-d
THF	D ₂ O	0	51	49
		-78	75	25
	CH ₃ OD	0	79	21
		-78	100	0
<i>t</i> -BuOD	0	100	0	
	-78	100	0	
Et ₂ O	D ₂ O	0	38	62

characterize H-4 α and H-4 β it was necessary to examine the NMR spectra of the diene adducts **4** and **5**.



The H-10 α and H-10 β of **4** give a distinct quartet well separated from the other proton signals. In **4** prepared from freshly monodeuterated **1**, the signals at δ 2.47 and 2.10 have an intensity ratio of 0.28 instead of 1.0 seen in undeuterated **4**. In the maleic anhydride adduct **5** a similar change is seen in the ratio of the intensities at δ 1.23 and 1.55. The assignment of these signals to the exo and endo hydrogens at position 10 in **4** was most clearly accomplished by the use of the lanthanide shift reagent tris[3-(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium (Eu(hfc)₃). This reagent, which complexes with the anhydride group,³ shifts the 1.55 and 1.23 signals by Δ Eu values of 2.45 and 5.80, respectively, indicating that the latter signal, corresponding to the preferred location of the deuterium, is α in **5** and on the endo or "under" face in **1**.

When dideuterated **1** was converted into **4**, the intensities of both the δ 2.47 and 2.10 peaks were seriously reduced with the almost complete disappearance of the absorption at δ 2.47.

In deuterium NMR, with CDCl₃ as reference, the D-4 α and D-4 β appeared as a single peak at δ 3.04–3.08, while D-3,5 was at δ 5.71–5.74.

Effects of Conditions on the Deuteration Product. Although deuteration of the lithium dienide from **1** at -78 °C with CH₃OD or *t*-BuOD yielded entirely **1** deuterated at the 4-positions at the diene ring, it was observed that the use of D₂O as a deuterium source gave a product including a new diene. This proved to be the previously unknown isomer **3**, deuterated at position 2 or 6.⁴ The new isomer can be produced in undeuterated form by the careful quenching of the lithium derivative with H₂O in THF or ether. Although **3** isomerizes readily to **1** on heating to 80 °C, it can be purified from a mixture by selective reaction of **1** with maleic anhydride at 0 °C, and **3** can be distilled at 15 °C (0.05 torr), having the same boiling point as its isomer. Thus in diene reactivity the isomers are in the order **2** \gg **1** $>$ **3**.

Table III compares the product compositions under different conditions of deuteration of the lithium derivative of **1**; it is seen

(3) Craig, R. E. R.; Craig, A. C.; Smith, G. D. *Tetrahedron Lett.* **1975**, 1189.

(4) The evidence for the structure and stereochemistry of the new isomer **3**, an account of its chemistry, and crystallographic evidence for the structure of its maleic anhydride adduct are included in a forthcoming publication in collaboration with W. H. Watson and J. Galloy.

Table IV. Thermal Rearrangement of Deuterium in Labeled **1** at 100 °C (0.1063 M in CCl₄)

time, min	composition, mole fraction					
	obsd values			calculated values ^a		
	D-4 α	D-4 β	D-(3 + 5)	D-4 α	D-4 β	D-(3 + 5)
0	0.816	0.174	0.010			
30	0.675	0.278	0.048	0.685	0.260	0.055
61	0.571	0.301	0.108	0.593	0.311	0.096
90	0.528	0.327	0.145	0.527	0.340	0.133
130	0.468	0.338	0.195	0.465	0.358	0.177
180	0.422	0.360	0.221	0.414	0.361	0.225
240	0.397	0.347	0.256	0.375	0.352	0.274
333	0.345	0.332	0.323	0.338	0.332	0.332
412	0.331	0.319	0.350	0.316	0.314	0.370
525	0.301	0.281	0.408	0.295	0.295	0.410
1510	0.256	0.253	0.491	0.251	0.251	0.498

^a Calculated on the assumption that: $k_{\alpha\beta} = k_{\beta\alpha} = k = 1.00 \times 10^{-4} \text{ s}^{-1}$; $k_{\alpha 3} = k_{\alpha 5} = k_{3\alpha} = k_{5\alpha} = k_{\beta 3} = k_{\beta 5} = k_{3\beta} = k_{5\beta} = k/(q + 1) = 1.33 \times 10^{-5} \text{ s}^{-1}$ and $q = 6.5$.

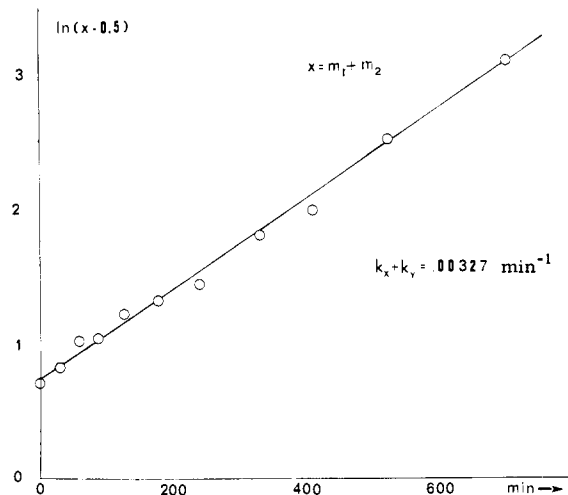


Figure 1. First-order plot of the reversible shift of deuterium from the 4- to the 3- and 5-positions in isodicyclopentadiene **1**. $x = (\text{D-4}\alpha + \text{D-4}\beta) =$ mole fraction of **1** deuterated at C-4.

that by the use of D₂O at 0 °C in ether, the new isomer can be had as 62% of the product.

Course of the Thermal Rearrangement of Deuterium in Labeled **1.** The redistribution of deuterium among the positions in the diene ring of **1** proceeded at a convenient rate at 100 °C, requiring almost 24 h to come to equilibrium. By following the ²H or the ¹H NMR spectra over this time interval, the distribution of deuterium between the 4- and the (3 + 5)-positions could be followed. At appropriate intervals, samples of the deuterated **1** were converted into the DMAD adduct, which required about 15–20 min at 10–15 °C in hexadeuterobenzene for complete disappearance of the original H-(3,5) peak. The ratio of the adduct peaks at δ 2.47 and 2.10 now gave the relative amounts of H-4 α and H-4 β . By combining this ratio with the checking results of the H and D NMR measurements on the reacting sample before derivatization, the mole fractions of D-4 α , D-4 β , and D-(3 + 5) could be determined, as tabulated in Table IV. The degree of deuteration of the sample, 1.02 D/molecule, could be checked by comparing the sum of the integrated intensities for H-4 α , 4 β , 3, and 5 with the sum for the unchanging H-1 and H-7 signals taken as an internal standard.

The only other detected reaction under these conditions was a slow dimerization of **1**. A rate study in chlorobenzene at 100 °C indicated a bimolecular rate constant of $1.8 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ for this dimerization. The importance of this competing reaction was minimized by carrying out the studies of the first-order sigmatropic shift at a diene concentration of 0.1 M.

A first step in studying the kinetics of the deuterium shift consists in treating the overall conversion of (D-4 α + D-4 β) into

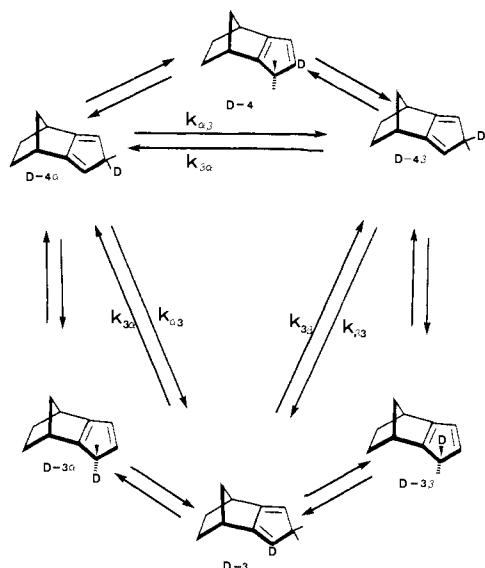


Figure 2. Elementary sigmatropic shifts involved in redistribution of deuterium among positions 4α , 4β , and 3 in isodicyclopentadiene **1**. The shifts involving position 5, not shown, are equivalent by symmetry of those involving position 3.^{12,13} The short arrows represent elementary hydrogen shifts; the long arrows correspond to the composite rate processes interconverting **1** structures differently labeled.

D-(3 + 5) as a reversible first-order process which can be treated without regard to the interconversion between D- 4α and D- 4β . Figure 1 shows a plot of $\ln(m_1 + m_2 - 0.5)$ against time, where m_1 is the mole fraction of D- 4α , m_2 is the mole fraction of D- 4β , and 0.5 is taken as the value of $(m_1 + m_2)$ at infinite time. The slope of the linear plot indicates that the sum of all the forward and reverse rate constants is $5.45 \times 10^{-5} \text{ s}^{-1}$.

The general pattern for the 1,5 sigmatropic shifts is shown in Figure 2, which includes all the possible locations of deuterium in the diene ring of **1** or **2** except those at position 5, which are equivalent by symmetry to the ones shown at 3. It is evident that each movement of D from one position to another in **1** is a sequence of two 1,5 sigmatropic shifts, one involving H and one involving D. The exception is the interconversion of D- 4α and D- 4β , which is accomplished by a 4-3 or 4-5 shift of H on one face of the ring and a return H shift on the other face. If every possible 1,5 sigmatropic shift had the same first-order rate constant, it would be consistent with the equilibrium composition $3:4\alpha:4\beta:5 = 1:1:1:1$. Two inequalities are indicated, however, by the experimental data: first, the shifts leading from the unsymmetrical diene structure **2** to the symmetrical diene structure **1** must be much faster than those in the other direction, since there is no detectable equilibrium concentration of the unsymmetrical dienes. The other inequality is indicated by the maximum (Figure 3) in the 4β concentration somewhere between 100 and 180 min, from which it follows that the rate constant for $4\alpha \rightleftharpoons 4\beta$ is faster than the others. These composite rate constants can differ only if the elementary k 's composing them are not all equal. Finally it is known⁵ that similar sigmatropic shifts are subject to substantial isotope effects. Thus, if k is the rate constant for a 1,5 shift of H originating in a symmetrical diene structure, we must at least allow for the inequalities $k/k_D = q$ and $k_u/k = v$, where k_u refers to shifts converting **2** to **1**. It is also possible that nonequivalence of the π orbitals on the two faces of the diene ring might give rise to unequal rates of sigmatropic shifts on the endo and exo faces. We have thus far found no indication of the magnitude of this effect, and we shall therefore test the applicability of a treatment based on the following assumptions. The notation for the rate constants is that defined by Figure 2. Assume the following:

All ^1H shifts converting bond structure **1** into **2** proceed with rate constant k .

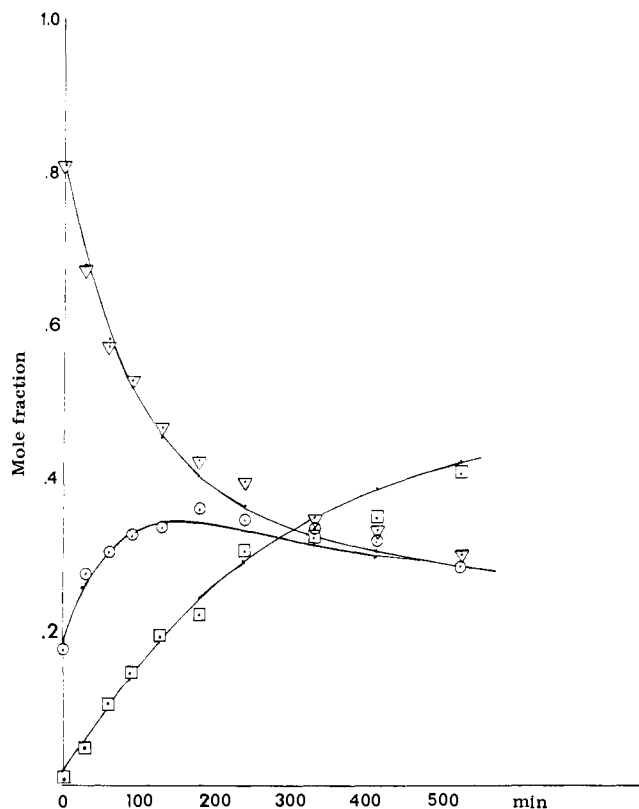


Figure 3. Course of the rearrangement of isodicyclopentadiene labeled with deuterium at 4α , determined in carbon tetrachloride at 100°C . Concentration of labeled **1**, 0.106 M. Triangles, mole fraction labeled at 4α ; circles, mole fraction labeled at 4β ; squares, mole fraction labeled at 3 + 5.

All deuterium shifts in this same direction have rate constant k/q .

Every shift leading from diene structure **2** to **1** has a rate constant v times that of the same shift going in the opposite direction.

These assumptions lead to the following relations among the rate constants. Every rate constant for the interconversion of two labeled **1** structures is the product of the rate constant for the first elementary shift by the probability of occurrence of the second required elementary shift, relative to simple reversal of the first. For example,

$$k_{\alpha 3} = \frac{k}{q} \frac{kv}{kv + (kv/q)} = \frac{k}{q + 1}$$

It is evident that by this scheme v always cancels out, since it is a factor of both numerator and denominator in the return ratio and appears nowhere else. This identifies the rate constants for the shifts within structure **1** as follows:

$$k_{\alpha\beta} = k_{\beta\alpha} = k$$

(since k is the sum of the constants for the conversion via D-3 and via D-5, each proceeding with rate constant $k/2$).

$$k_{\alpha 3} = k_{\alpha 5} = k_{3\alpha} = k_{5\alpha} = k_{\beta 3} = k_{\beta 5} = k_{3\beta} = k_{5\beta} = k/(q + 1)$$

In the kinetic treatment shown in Figure 1,

$$\begin{aligned} -\frac{d(D_{4\alpha} + D_{4\beta})}{dt} &= (k_{\alpha 3} + k_{\alpha 5})(D_{4\alpha}) + (k_{\beta 3} + k_{\beta 5})(D_{4\beta}) - \\ &\quad (k_{3\alpha} + k_{3\beta})(D_{3\alpha} + D_{3\beta}) - (k_{5\alpha} + k_{5\beta})(D_{5\alpha} + D_{5\beta}) \\ &= \frac{2k}{q + 1}(D_{4\alpha} + D_{4\beta}) - \frac{2k}{q + 1}(D_{3\alpha} + D_{3\beta} + D_{5\alpha} + D_{5\beta}) \\ &= \frac{2k}{q + 1}(D_{4\alpha} + D_{4\beta}) - \frac{2k}{q + 1}[1 - (D_{4\alpha} + D_{4\beta})] \\ &= \frac{4k}{q + 1}(D_{4\alpha} + D_{4\beta}) - \frac{2k}{q + 1} = \frac{4k}{q + 1}[(D_{4\alpha} + D_{4\beta}) - 0.5] \end{aligned}$$

Thus the first-order rate constant from the slope of the line in Figure 1 is equal to $4k/(q+1)$, so that $k/(q+1) = 1.36 \times 10^{-5} \text{ s}^{-1}$.

Under the set of assumptions that we are testing, a determination of k will make it possible to evaluate the isotope effect q for an elementary sigmatropic shift, and to test the treatment by using the values of the two rate constants to determine the concentrations of D4 α , D4 β , D3, and D5 as a function of time, comparing them with the observed values in Figure 3. This was done by first estimating $k_{\beta\alpha}/(k_{\beta\alpha} + k_{\beta\delta})$ from the values of the variables at 180 min, where D4 β appears to be a maximum. Since the location of this maximum is not very precise, a series of approximations was made until values of the two rate constants were found which gave satisfactory curves of D4 α , D4 β , and D(3+5) as functions of time. The calculations were made from the differential equations for the simultaneous interconversions of the isotopic isomers, using a computer program to approximate the integrations with a series of 170 small time increments. The curves of Figure 3 are the result of this calculation using the two rate constants 1.33×10^{-5} and 10.0×10^{-5} . There are no deviations in the fit suggesting any gross error in the assumptions. It appears, therefore, that $q+1 = 7.5$ and the kinetic isotope effect ($q = 6.5$) is the reason for the interconversion of D- α and D- β being faster than any of the other isomerization rate constants.¹⁰

Discussion

The strong preference for lithium isodicyclopentadienide for deuteration at position 4 is obviously related to the electronic structures of the anion and the hydrocarbon **1**. As indicated by the NMR spectra (Tables I and II) the anion has its delocalized charge rather evenly distributed among carbon atoms 3, 4, and 5. As is known from the preference for structure **1** over the isomers **2** and **3**,^{1,6} the attachment of H or D at position 4 is more exothermic than at 3 or 5, and this point of attack has greater inherent probability. The choice between the α and β faces of the ring can be related to the location of the lithium ion and in turn to the steric environments on the two faces and to the corresponding π orbital extension above and below the ring plane.

Attention has been called^{7,8} to the unequal interaction of the π orbitals of *syn*-sesquiorbornene with the methylene compared to the ethylene bridges, and its relation to the presence or absence of a node in the HOMO of this system. The exclusive exo selectivity of **2** toward dienophiles compared to **1** has been correlated with the absence in **2** of the node which in the HOMO of **1** allows a greater upward bend at the junction of the saturated and unsaturated rings.¹ Compared to the molecule **2**, with the space over C₂-C₆ continuously occupied in two bonding orbitals, the dienide ion might have slightly more of an upward bend and might slightly favor π orbital extension and association with lithium on its α -(endo) face.¹¹ The evidence is, however, that access of H and

D donors to both faces is balanced enough so that the product is importantly determined by solvent and temperature. If both faces of the diene ring are equally accessible, there is a simple reason why the observed selectivities might occur.

Given the great preference for attack at C-4, the choice is between β approach directly over C-4 in the space adjacent to the methylene bridge hydrogen H-10, or on the opposite α face in the space between H-8(endo) and H-9(endo). The differently spaced hydrogen atoms could easily produce the 4.7-fold difference between α - and β -deuteration.

This speculation applies to the deuteration with alcohols, in which no attack at C-2 or C-6 is observed. It is of interest that the smallest possible deuteration agent, D₂O, begins to show competing deuteration at the more hindered position (2 or 6) at the ring junction, and that this attack shows an appreciably higher activation energy (estimated ($E_6 - E_4$), 1.4 kcal). Such marginal close-range effects of hydrogen would be self-consistent and in the right direction to explain the observations. Just as the locations in space of H-8, H-9, and H-10 should lead to a preference for 4-deuteration on the α face, so these same hydrogen atoms should favor the β face for deuteration at C-2 or C-6, where the choice is β entry staggered with H-10 or α entry eclipsed with H-8 or H-9. Thus this hypothesis fits well with that of closely similar general reactivity on the α and β faces of the diene system.

As to the diene reaction of **3**, since the unsaturated ring is distorted and twisted in the endo direction by the sp³ bonding at C-6, it is to be expected that dienophiles will attack on the exo face as observed, while the "Alder's rule" orientation of the maleic anhydride ring⁴ is expected from both orbital overlap and bridge hindrance. Finally, these considerations make it obvious why the Diels-Alder reactivities of **1** and **2** are parallel to the instabilities of their strictly planar diene systems, whereas this is not the case with the Diels-Alder reactivities of **1** and the nonplanar **3**, the key factor in the separability of **1** and **3**.

The situation of the shiftable hydrogen in **2** is geometrically similar to that in **1**, since the diene systems in both isomers are coplanar. In **3**, however, a torque is imposed by the location of the saturated carbon at the ring junction, and this must be relatively unfavorable for the shift $6 \rightarrow 5 \beta$ which converts **3** into **2** and which is a necessary first step in return to a deuterated **1**. Thus all the special features of **3**— the conditions of its formation, the β location of its H or D, its facial selection in the diene reaction, and its position in the thermal stability series **1** > **3** > **2**— can be viewed as consequences of a π system fused to a norbornyl system and available to reaction on both faces.

Experimental Section

Isodicyclopentadiene **1** was prepared as described elsewhere.⁶ Dimethyl acetylenedicarboxylate, deuterium oxide (99.9%), methanol-*d* (99.5%), 2-methyl-2-propanol-*d* (98%), and dimethyl-*d*₆ sulfide (99.9%) were purchased from Aldrich Chemical Co. and used without further treatment. Maleic anhydride was purified by sublimation from purchased products.

¹H NMR spectra were obtained on a Varian EM-390 90-MHz spectrometer. ¹³C NMR spectra were obtained on a JEOL FX-60 (15 MHz) spectrometer. ²H NMR spectra were also recorded on the JEOL FX-60 spectrometer at 9.18 MHz, using CDCl₃ (δ 7.24) as internal standard. Gas chromatography was performed on a Perkin-Elmer Sigma-3 chromatograph, using a 6-ft column packed with 5% SE-30 on Chromosorb W-AW 60-80 mesh. Mass spectra were determined on Finnigan OWA 1020 GC-MS-DS, using a 6-ft column packed with 5% Carbowax 20 M on Chromosorb W-AW 60-80 mesh; the ionization potential is 70 eV. Melting points are uncorrected.

LIS reagents used were tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium, Eu(fod)₃, and tris[(3-(heptafluoropropyl)hydroxymethylene)-*d*-camphorato]europium, Eu(hfc)₃, both purchased from the Aldrich Chemical Co. Shifts of peaks were followed on stepwise addition of LIS reagents to the test CDCl₃ solution up to 0.2:1 of reagent:substrate mole ratio, the Δ Eu values are $\Delta\delta$ values extrapolated to 1:1 mole ratio.

Monodeuterated Isodicyclopentadiene 1. A. Deuteration by Deuterated Alcohols. To a stirred solution of 1.0 g (7.5 mmol) of isodicyclopentadiene **1** in 15 mL of THF was slowly added 5.5 mL (7.5 mmol) of *n*-butyllithium solution (1.37 M in hexane) at 0 °C and under argon. After 1 h, the reaction mixture was cooled in a dry ice bath and 2 mL

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

(7) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022.

(8) Bartlett, P. D.; Roof, A. A. M.; Winter, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 6520.

(9) Takahashi, K.; Takase, K.; Kagawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 1186.

(10) A similar value of k_H/k_D , 7.6, is obtained by extrapolating to 100 °C the vapor-phase data obtained by Roth and König (ref 5) for the 1,5 sigmatropic shift in the open-chain analogue, 1,3-pentadiene-5-*d*₂ and 1,3-pentadiene-1-*d*₂. A quite symmetrical transition state is considered to be a prerequisite for such a high isotope effect in a sigmatropic reaction (cf, ref 14).

(11) However, in the formation of bis(η^2 -isodicyclopentadienyl)nickel(II), the metal atom is sandwiched between the β faces where the bridge hindrance is less: Scroggins, W. T.; Rettig, M. F.; Wing, R. M. *Inorg. Chem.* **1976**, *15*, 1381.

(12) Similarly, isomer **2** deuterated at vinylic position 3 is not included in Figure 2 since it is not an intermediate in any of the position shifts of deuterium.

(13) Although the isotopic species here referred to as D-3 and D-5 are enantiomers, the emphasis in this discussion is on the doubled probability of a sigmatropic shift from 4 α or 4 β when the hydrogen can move equivalently to either of two new positions.

(14) Mironov, V. A.; Fedorovich, A. D.; Akhrem, A. A. *Russ. Chem. Ref. (Engl. Transl.)* **1981**, *50*, 666.

of CH₃OD was slowly added. Stirring was continued for 6 h while the temperature of the reaction mixture was slowly raised to room temperature. The mixture was poured onto crushed ice and worked up with ether. The organic layer, after being dried over MgSO₄ and evaporated on a rotary evaporator at room temperature and diminished pressure for 2 h, was vacuum transferred at 20 °C (0.05 torr) to give 0.8 g of monodeuterated **1** (80% yield): GC analysis at 100 °C gives only one peak (>98%); GC-MS, gives *m/e* 133 (M⁺), 118, 116, 105, 104, 92, 79, 78, 66, 63. All major mass fragments are 1 unit larger than the corresponding nondeuterated ones. ¹H NMR (C₆D₆) δ 5.65 (d, 2 H, *J* = 1.5 Hz, H₃, H₅), 3.10 (m, 1 H, H₄), 2.95 (m, 2 H, H₁ and H₇), 1.2–1.8 (m, 6 H, H₁, H₇, H₈ and H₉); ¹³C NMR (CDCl₃) δ 155.8 (s, C₂ and C₆), 113.9 (d, C₃ and C₅), 46.1 (t, C₁₀), 44.9 (t, ¹*J*_{CD} = 19 Hz) (d, C₄), 38.5 (d, C₁ and C₇), 28.5 (t, C₈ and C₉); ²H NMR (CCl₄) δ 5.71 (D₃ and D₅, 3.5%), 3.08 (D₄, 96.5%).

Composition of **1** as a mixture of D-4α, D-4β, and D-(3 + 5): The ratio of (D-4α + D-4β)/D(3 + 5) is determined by ²H NMR directly or by ¹H NMR, measuring residual H₄/H(3 + 5) ratio using the H(1 + 7) peak as internal standard or a CH₃NO₂ fraction as external standard. C₆D₆ was used as solvent to reduce the overlapping of H₄ and H(1,7). The ratio of H₄α/H₄β is determined as follows. To a solution of 50 mg of **1** in 300 μL of C₆D₆ was added 50 μL of DMAD at 10–15 °C. The ¹H NMR spectrum was taken after the total disappearance of the H(3,5) peak, usually 15–20 min. ¹H NMR of **4** (C₆D₆) δ 3.85 (br s, 8 H, H₁, H₄, and methyl), 3.05 (br s, 2 H, H₅ and H₈), 2.47 (dt, *J* = 7.0 and 1.8 Hz, 1 H, H₁₀α), 2.10 (dt, *J* = 7.0 and 1.8 Hz, 1 H, H₁₀β), 1.45 (m, 3 H, H₆β, H₇β, and H₉β), 1.10 (dt, *J* = 8.4 and 1.5 Hz, 1 H, H₉α), 0.55 (m, 2 H, H₆α and H₇α). ¹³C NMR of **4** (CDCl₃) δ 166.0 (s, carbonyl), 158.7 (d, C₂ and C₃), 150.3 (s, C₄α and C₈α), 69.9 (t, C₁₀), 52.0 (q, methyl), 48.5 (t, C₉), 42.9 (d, C₁, C₄, C₅, and C₈), 22.3 (t, C₆ and C₇).

The ratio of H₁₀α (δ 2.47)/H₁₀β (δ 2.10) in **4** corresponds to H₄α/H₄β in **1**. From the (D-4α + D-4β)/D(3 + 5) and D₄α/D₄β ratio, the composition of **1** is calculated (D-4α, 79.5%; D-4β, 17.0%; D-(3 + 5), 3.5%). Extent of deuteration is 1.05 deuterium per molecule as measured by the external standard method.

Deuteration by *t*-BuOD gave similar results: monodeuterated **1**, 80% yield; composition: D-4α, 85%; D-4β, 13%; D(3 + 5), 2%.

B. Deuteration by Deuterium Oxide. D₂O (2 mL) in THF (5 mL) was used instead of CH₃OD (2 mL) in the above experiment (A) at –78 °C. Other manipulations are the same. Product (0.6 g) (60% yield) was obtained after vacuum transfer. GC analysis at 100 °C gives only one peak. ¹H and ¹³C NMR spectra are a superposition of **1** and **3** (described below). The composition of **1** is as follows: D-4α, 83% D-4β, 15%; D-(3 + 5), 2%. The ratio of **1** to **3** as measured by ¹H NMR is 75/25. When a solution of the product in C₆D₆ was heated in the NMR probe at 100 °C for 10 min, all **3** signals disappeared.

When the above experiment is performed at 0 °C and with Et₂O instead of THF, the product is a mixture of 38% **1** and 62% **3**.

Dideuterated 1. The procedure used for preparation of monodeuterated **1** was repeated several times on the same sample. From 5 g of **1** (38 mmol), the deprotonation–deuteration–ether workup–vacuum transfer sequence was repeated 5 times. Product (1.1 g) (21% yield) was obtained. D₄/D(3 + 5) ratio is 74/26 (²H NMR method), 76/23 (¹H NMR external standard method). Extent of deuteration is 2.28 deuterium atoms per molecule. (H₄ 86% deuterated, H₃ and H₅ 29% deuterated).

Cycloadducts (5) of Maleic Anhydride with Nondeuterated and Deuterated 1. Procedures follow the description in ref 7. From each 1 g of **1** (nondeuterated or deuterated), 0.4 g of syn-exo-cycloadduct crystals (**5**) was separated.

The δ values, Δ*E*_u values with Eu(hfc)₃, and assignments of ¹H NMR spectrum of **5** are respectively: δ 3.33, 4.25, H₁ and H₄; 2.95, 0.70, H₅ and H₈; 2.50, 5.50, H₂ and H₃; 1.55, 2.45, H₁₀β; 1.55, 0.25, H₆β and H₇β; 1.37, 0.50, H₉β; 1.23, 5.80, H₁₀α; 1.02, 0.40, H₉α; 0.59, 0.95, H₆α and H₇α. The intensity ratios of H₁₀α to H₁₀β for cycloadducts of nondeuterated and deuterated **5** are 1.0 and 0.32, respectively.

Preparation of Undeuterated Diene 3. To a stirred solution of 4.0 g (30 mmol) of **1** in 30 mL of Et₂O was slowly added 22.1 mL of *n*-bu-

tyllithium solution (1.37 M in hexane). After 1 h, 10 mL of H₂O was slowly added to this mixture and stirred for another 2 h. The reaction mixture was cooled in an ice bath during the whole addition period. The mixture was poured into ice water and worked up with ether. After the mixture was dried with MgSO₄ and ether evaporated at room temperature, the mixture was vacuum transferred at 20 °C (0.05–0.1 torr), giving 2.9 g of product. ¹H NMR showed this to be a binary mixture of 38% **1** and 62% **3**. This product mixture was added to 0.97 g (10 mmol) of maleic anhydride dissolved in 5 mL of CH₂Cl₂ and cooled in an ice bath. The mixture was stirred for 2 h and CH₂Cl₂ was evaporated at 0 °C. The viscous liquid was then passed quickly through a short column packed with silica gel (Baker) and eluted with pentane. The eluate, after evaporation of the solvent at 0 °C, was vacuum-transferred at 10 °C (0.05 torr) to give 1.2 g of **3** (30% yield) which is free from **1**. Upon standing at room temperature, **3** slowly isomerized to **1** with partial polymerization: ¹H NMR (CDCl₃) δ 6.65 (m, 1 H), 6.08 (m, 2 H), 3.25 (m, 1 H), 3.13 (m, 1 H), 2.72 (m, 1 H), 0.3–1.7 (m, 6 H); ¹³C NMR (CDCl₃) 166.5 (s), 138.7 (d), 130.2 (d), 122.5 (d), 69.5 (d), 43.0 (t), 40.7 (d), 40.2 (t), 39.8 (d), 21.6 (t).

Monodeuterated 3. Deuterium oxide was used instead of H₂O in the above example, while other conditions were identical. From 2.0 g (15 mmol) of **1** was obtained 0.5 g of monodeuterated **3** (20% yield), NMR spectra identical with those the nondeuterated **3** except δ 3.25 in the ¹H NMR spectrum is missing and δ 69.5 in the ¹³C NMR spectrum is split into three peaks.

Isodicyclopentadienide Anion. A. Sodium Salt. Pentadeuteriodimethyl sodium was prepared by the literature procedure.⁹ **1** (260 mg, 2 mmol) was added to a solution of pentadeuteriodimethylsodium (2 mL, 1.53 M) in Me₂SO-*d*₆ under argon at 0 °C. No residual peaks of **1** were observed in the ¹H or ¹³C NMR spectra: ¹H NMR δ 5.06 (1 H, AB₂, *J*_{3–4} = 2.7 Hz, H₄), 4.98 (2 H, AB₂, H₃ and H₅), 2.93 (2 H, br s, H₁ and H₇), 1.58 (2 H, m, *J*_{3α–3β} = 5.0 Hz, H₈β and H₉β), 1.46 (1 H, m, *J*_{10α–10β} = 6.8 Hz, H₁₀α), 1.32 (1 H, m, *J*_{9α–10β} = 1.0 Hz, H₁₀β), 0.68 (2 H, m, H₈α and H₉α); ¹³C NMR (Me₂SO-*d*₆) δ 127.8 (s, C₂ and C₆), 102.4 (d, C₄, ¹*J*_{CH} = 151 Hz), 93.0 (d, C₃ and C₅, ¹*J*_{CH} = 142 Hz), 51.0 (t, C₁₀, ¹*J*_{CH} = 134 Hz), 41.1 (d, C₁ and C₇, ¹*J*_{CH} = 146 Hz), 30.8 (t, C₈ and C₉, ¹*J*_{CH} = 130 Hz).

B. Lithium Salt. *n*-Butyllithium (3.3 mL, 1.37 M in hexane) was added to Me₂SO-*d*₆ (3 mL) under argon and the mixture was stirred at room temperature for 0.5 h. To this mixture was added 530 mg (4 mmol) of **1** and stirring was continued for another 0.5 h. Hexane and butane were pumped off at room temperature (2 torr): ¹H NMR (Me₂SO-*d*₆) δ 4.94 (1 H, AB₂, *J*_{3–4} = 2.6 Hz, H₄), 4.89 (2 H, AB₂, H₃ and H₅), 2.90 (2 H, br s, H₁ and H₇), 1.57 (2 H, m) 1.48 (1 H, m), 1.30 (1 H, m), 0.68 (1 H, m); ¹³C NMR (Me₂SO-*d*₆) 127.5 (s), 102.1 (d), 93.2 (d), 51.2 (t), 40.9 (d), 30.8 (t).

Rates of Dimerization of 1. A 1-mL solution of **1** (2.0 M) and dodecane (0.7 M) in chlorobenzene was put in a rubber-capped vial. After the solution was degassed by argon bubbling, the vial was put in an oil bath (100 ± 0.1 °C) and aliquots were taken and analyzed by GC, using dodecane as the internal standard. The reaction rate follows second-order kinetics up to 90% conversion. Rate constant *k*₂ = 1.80 × 10^{–3} s^{–1} M^{–1} was obtained by regression analysis.

Rates of Sigmatropic Reaction of Monodeuterated 1. Aliquots (15 mL) of 0.1 M monodeuterated **1** in CCl₄ were sealed in ampules under argon. The carbon tetrachloride had been distilled under argon. The ampules were put in an oil bath at 100 ± 0.1 °C and quenched in ice water when drawn out. The heated samples were vacuum-transferred at 20 °C (0.05 torr) before analysis which was as described above. The composition of the heated sample as a mixture of D-4α, D-4β, and D-(3 + 5) vs. time is shown in Table IV.

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Registry No. **1**, 6675-72-5; **1** anion, 83877-21-8; **1** anion-Na⁺, 83877-22-9; **1** anion-Li⁺, 83877-23-0; **2**, 75725-33-6; **3**, 83877-20-7; **4**, 82918-66-9; **5**, 83944-26-7; DMAD, 762-42-5; maleic anhydride, 108-31-6; deuterium, 7782-39-0; hydrogen, 1333-74-0.