

# Studies in Stereochemistry. XLI. Stereochemical Course of Thermal Isomerization in the Indene System<sup>1</sup>

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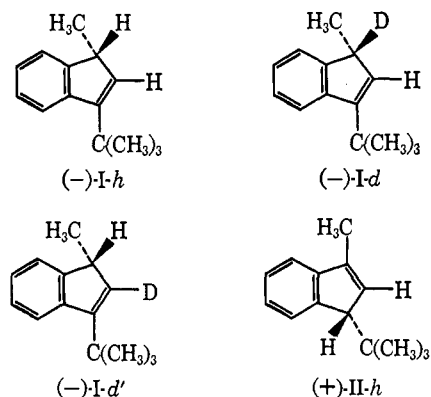
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**Abstract:** The stereochemical course of thermally induced hydrogen migrations in an indene system in the liquid phase has been examined. Optically pure samples of (–)-1-methyl-3-*t*-butylindene ((–)-I-*h*), 1-methyl-3-*t*-butylindene-1-*d* ((–)-I-*d*), and (–)-1-methyl-3-*t*-butylindene-2-*d* ((–)-I-*d'*) when heated to 140°, neat, partially isomerized to 3-methyl-1-*t*-butylindene (II-*h(d)*). The resulting mixtures (far from being equilibrated) were separated, and the samples of I and II were analyzed for optical purity. The product II-*h*, isolated from isomerization of (–)-I-*h* was 99% racemic, and the 1% remainder possessed the configuration predicted by an overall suprafacial hydrogen shift ((–)-I → (+)-II). The near racemic character of II strongly supports the intervention of the optically inactive isoindene intermediate of type A in the major reaction. The small residual activity is accommodated by the less-favored occurrence of optically active intermediates of types B and C in the production of a small fraction of II. Starting material deuterated in the 1 position ((–)-I-*d*) isomerized a factor of 3 slower than (–)-I-*h*, and after 13.5% isomerization gave II, 48% optically pure. The optically active component possessed the configuration predicted by an antarafacial hydrogen shift ((–)-I → (–)-II). This result pointed to a deuterated, optically active isoindene intermediate (type A, monodeuterated) whose hydrogen in the 2 position completed the migration (started by deuterium) faster than did the deuterium due to a kinetic isotope effect of about 2.9. Optically pure (–)-I-*d'* (deuterium in the 2 position) was prepared and 22% isomerized to II, which was 42% optically pure, and whose optically active component possessed a configuration in which the benzyl hydrogen or deuterium possessed a configuration suprafacially related to that of starting material. This result pointed to a kinetic isotope effect of 2.7 for the formation of II from deuterated intermediate A.

Studies of thermal hydrogen shifts across conjugated  $\pi$ -electron systems have been reviewed,<sup>2</sup> and their occurrence and stereochemical course have been correlated in terms of the symmetry properties of their highest occupied molecular orbitals.<sup>2a</sup> Accordingly, indene has been shown<sup>3</sup> to undergo a thermal [1,5]-sigmatropic shift<sup>4</sup> through the reactive intermediate isoindene detected by deuterium-labeling experiments<sup>3a</sup> and by isolation of its maleic anhydride adduct.<sup>3b</sup> In a recent study of phenyl-substituted indenenes,<sup>5</sup> hydrogen was found to undergo thermal shifts faster than the phenyl group, which in turn, migrated faster than the methyl group.

As part of previous studies, the relative configurations and maximum rotations of (–)-1-methyl-3-*t*-butylindene ((–)-I-*h*), (–)-1-methyl-3-*t*-butylindene-1-*d* ((–)-

I-*d*), and (+)-3-methyl-1-*t*-butylindene ((+)-II) were reported.<sup>6</sup> In addition, (–)-methyl-3-*t*-butylindene-2-*d* ((–)-I-*d'*) was prepared.



These systems offer special advantages for the study of thermal hydrogen shifts. (1) Although base-catalyzed isomerization of I to II occurs at much lower temperatures,<sup>6</sup> this reaction can be avoided by special washing and drying of equipment, and the thermal rearrangement occurs in the neat state at a convenient rate at 140°. (2) At 140° the equilibrium constant for  $I \rightleftharpoons II$  is estimated by extrapolation of the data gained in nonpolar solvents<sup>6a</sup> to be 5.5. Thus, the forward reaction of I → II can be studied without the complications of the reverse reaction if the disappearance of I is not carried past a half-life. (3) In the absence of oxygen and light, no side reactions can be detected. (4) The differences in symmetry properties of tetraenes

(1) This investigation was supported by the U. S. Public Health Service Research Grant No. GM12640-05 from the Department of Health, Education, and Welfare.

(2) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965); (b) W. R. Roth, *Chimia*, **20**, 229 (1966); O. Cervinka and O. Kriz, *Chem. Listy*, **62**, 321 (1968).

(3) (a) W. R. Roth, *Tetrahedron Lett.*, 1009 (1964); (b) J. A. Berson and G. B. Aspelin, *Tetrahedron*, **20**, 2697 (1964); (c) K. Alder, F. Pascher, and H. Vagt, *Chem. Ber.*, **75**, 1501 (1942); (d) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).

(4) In this paper the terms 1,2- or 1,3-hydrogen shift or migration will be used in the conventional way, where the atoms are numbered along the shortest atomic chain between the migration origin (atom 1) and terminus. Thus, a 1,4-shift denotes a migration from atom 1 to atom 4, over a 3-bond system which forms the most direct path between 1 and 4. This method of numbering is mechanism independent, and was employed as early as 1922 [A. Gillet, *Bull. Soc. Chim. Belg.*, **31**, 365 (1922)] and later used prominently in G. W. Wheland's text [*Advanced Organic Chemistry*, 3rd ed, John Wiley & Sons, Inc., New York N. Y., 1960, p 536]. The system in no way utilizes the conventional numberings of carbon skeletons of frequently mentioned bi- or polycyclic compounds, nor does it describe the  $\sigma$ - $\pi$  bond interchanges that often accompany the shift. When such interchanges are also designated, the [m,n]-sigmatropic shift mechanistic nomenclature will be employed.

(5) L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Amer. Chem. Soc.*, **91**, 1578 (1969).

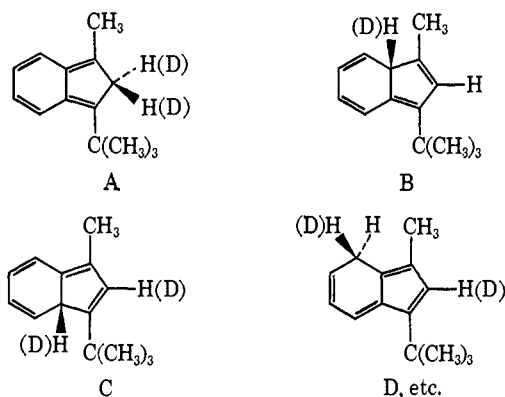
(6) (a) J. Almy and D. J. Cram, *ibid.*, **91**, 4459 (1969); (b) J. Almy, R. T. Uyeda, and D. J. Cram, *ibid.*, **89**, 6768 (1967). Syntheses of (±)-II and (–)-I were also reported by (c) A. Weidler, *Acta Chem. Scand.*, **17**, 2724 (1963); (d) A. Weidler and G. Bergson, *ibid.*, **18**, 1483 (1964).

**Table I.** Stereochemical Outcome of Isomerizations at  $140 \pm 1^\circ$  of Neat Liquid Samples of (–)-1-Methyl-3-*t*-butylindene ((–)-I-*h*), 1-Methyl-3-*t*-butylindene-1-*d* ((–)-I-*d*), and (–)-1-Methyl-3-*t*-butylindene-2-*d* ((–)-I-*d'*) to 3-Methyl-1-*t*-butylindene (II-*h*(*d*))

Run no.	Starting material	<i>T</i> , hr	$k_i \times 10^6$ , sec <sup>-1</sup> <sup>a</sup>	I			II			
				Obtained, %	Optical purity, % <sup>b</sup>	Atom of H, % <sup>c</sup>	Obtained, % <sup>b</sup>	Optical purity, % <sup>b</sup>	Sign of rotation	Atom of H, % <sup>c</sup>
1 <sup>d</sup>	(±)-I- <i>h</i>	408	0.69	41			59			
2	(–)-I- <i>h</i>	284	0.60	56.5	54.6		43.5	1	+	
3	(–)-I- <i>h</i> <sup>e</sup>	261	0.65	57.5	53.0		42.5	1	+	
4	(–)-I- <i>d'</i>	190	0.20	86.5	87.8	10 ± 4	13.5	47.9	–	81 ± 4
5	(–)-I- <i>d'</i> <sup>d, g</sup>	96	0.74	78	85.4	89 ± 4	22	42.4	+	77 ± 4
6	(–)-I- <i>h</i>	277	0.84	47			53			
7	(–)-I- <i>h</i> <sup>e</sup>	277	0.76	50			50			

<sup>a</sup> One-point first-order rate constants. Rate of isomerization calculated from the equilibrium condition, 15.5% of I, 84.5% of II at 140°. <sup>b</sup> Based on  $[\alpha]^{25}$  (obsd) at four wavelengths, *c* 0.5, chloroform, 1-dm tube. <sup>c</sup> Per cent of one atom of H at benzyl position as measured by nmr analyses. <sup>d</sup> Sample contained tetradecane as internal standard, and glpc showed 100% recovery of I + II. <sup>e</sup> Ampoule rinsed last with 10% ammonia before water rinse prior to use. All other ampoules rinsed last with dilute acetic acid before rinse (see Experimental Section). <sup>f</sup> 0.995 atom of deuterium per molecule (mass spectral analysis). <sup>g</sup> 0.93 atom of deuterium per molecule (nmr analysis). Isomerization data are uncorrected for incomplete deuteration.

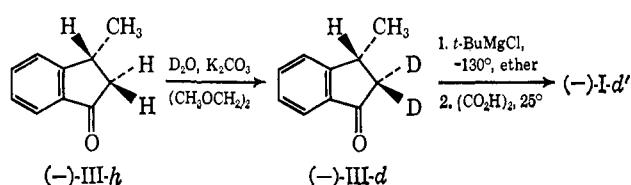
A, B, C, and D allow them to be largely differentiated as possible intermediates by examination of the optical purity and configurations of II produced from (–)-I-*h*, (–)-I-*d*, and (–)-I-*d'*. Ultimately, any optically active



II produced from I *via* appropriately deuterated A would depend on the kinetic isotope effect for hydrogen *vs.* deuterium migration to complete the overall conversion.

## Results

**Starting Materials.** The preparation, determination of configurations, and maximum rotations of (–)-I-*h*, (–)-I-*d*, and (–)-II-*h* have been described previously.<sup>6a</sup> For preparation of (–)-I-*d'*, 3-methylindanone (–)-III-*h* of maximum rotation and known configuration<sup>6</sup> was subjected repeatedly to potassium carbonate catalyzed isotope exchange with deuterium oxide to give (–)-III-*d*, which was converted to (–)-I-*d'* by a published procedure.<sup>6a</sup> The optical purity of (–)-III-*d* (and therefore of (–)-I-*d'*) was demonstrated by re-exchange of (–)-III-*d* with protium oxide to provide (–)-III-*h* of the same rotation as that used to form (–)-III-*d*.<sup>6a</sup> Analysis of (–)-I-*d'* using nmr techniques demonstrated it to be 93% deuterated in the 2 position.



**Thermal Isomerization.** Neat samples of (–)-I-*h*, (–)-I-*d*, and (–)-I-*d'* were heated in the absence of oxygen at 140° until isomerization was from 13 to 59% complete. The components of each run were then separated by glpc,<sup>6a</sup> and the optical activity of recovered I and II determined. Nuclear magnetic resonance spectra of the purified samples of I and II were taken in runs 4 and 5 (Table I). Integrals of the proton in the benzyl region compared to those for the aromatic, methyl, and *t*-butyl signals were determined. Table I summarizes the times employed, the relative amounts and rotations of I and II obtained with the percentages of one atom of hydrogen in the methine (benzyl) position, and the calculated one-point rate constants for I → II in each run. In run 1, (±)-I was used mixed with tetradecane as an internal standard, and the results demonstrated that the combined amounts of I and II produced accounted for 100% of the starting material. Comparisons of the rate constants for runs 1 and 2 and runs 6 and 7 indicate there was virtually no difference in isomerization rate between runs in which the glass ampoules used were exposed last to acetic acid or ammonia before rinsing and drying prior to use. Earlier experiments with less well-washed equipment led to large rate increases and nonreproducible stereochemical results. Extrapolation of equilibrium data for I ⇌ II (obtained at three temperatures in three different solvents for the base-catalyzed process)<sup>6a</sup> to 140° gave 15.5% of I and 84.5% of II. These values served as a basis of calculation of one-point rate constants ( $k_i$ ) for the isomerization of I → II. A rough  $k_b/k_a$  ratio for isomerization based on runs 3 and 4 is  $3 \pm 1$ . The maximum isotope effect is about 5.0 at 140°. The value of our isotope effect is very approximate, both because it depends on one-point rate constants and because temperature control at 140° was good only to 1°. Product II from run 2 had  $\alpha_{365}^{25}$  (observed) of only 0.006° (*c* 0.3, chloroform, 1 dm), whereas the probable error for the polarimeter is  $\pm 0.005^\circ$ . To confirm the inference that the small positive rotation was due indeed to (±)-II, an optical rotatory dispersion spectrum of the sample was taken, and was found to conform to that of authentic material. The intensity of the Cotton effect was 1% of that of optically pure

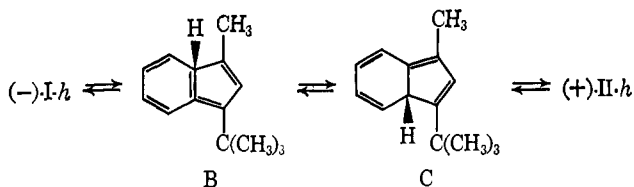
(7) (a) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960, p 22; (b) see, however, W. R. Roth and J. König, *Ann.*, **699**, 24 (1966).

(+)-II. Because of hydrogen-deuterium exchange of the vinyl proton during preparative glpc (see Experimental Section), exchange data from both nmr of the vinyl region and mass spectra were not used for our determinations in Table I or elsewhere. However, this incidental exchange was small (2–3% for each glpc pass), and the apparent loss of deuterium by mass spectrometry could be accounted for. These facts support Berson's conclusion<sup>3b</sup> that the indene-isoindene interconversion is intramolecular.

## Discussion

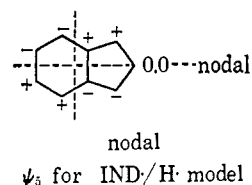
**Stereospecificity in the Isomerization Reaction.** The product II from (–)-I-*h* in run 2 was about 99% racemic. This result indicates that the major reaction mechanism involved an optically inactive intermediate such as A or D of which A is by far the more probable. This conclusion is in concert with the results of Berson, *et al.*,<sup>2b</sup> who captured isoindene (A without the alkyl groups) as a reaction intermediate with the dienophile, maleic anhydride (20% overall yield from indene itself). That D does not occur as a minor intermediate is not altogether ruled out, either by our results or those of others. However, integrations of the aryl signals for I and II, after runs 4 and 5, showed no perceptible exchange indicating that pathways utilizing D as an intermediate are of little importance, if any.

The 1% of optically pure (+)-II produced in run 2 is formally the product of an overall suprafacial 1,3-hydrogen transfer. Several stereospecific pathways can be envisioned to account for this reaction component: (1) a reaction catalyzed by the glass surface; (2) a one-stage photochemical [1,4]-sigmatropic hydrogen shift; (3) a one-stage thermal [1,4]-sigmatropic hydrogen shift ((–)-I → (+)-II); (4) a series of thermal [1,5]-sigmatropic shifts along the bridgehead carbon atoms of the indene system ((–)-I-*h* → B → C → (+)-II-*h*). Of the possibilities mentioned, (2) seems the least likely. Samples of (–)-I-*h* remained stable to isomerization for months during intermittent exposure to ordinary light. Although possibility (1) cannot be ruled out, the reproduction of results in runs 2 and 3 using ampoules differently rinsed suggests that wall-catalyzed reaction routes are improbable. The best and most interesting possibilities are (3) and (4). Mechanism (4) resembles the main reaction path (see below) except that it involves optically active intermediates B and C instead of optically inactive A, and three instead of two 1,2-hydrogen shifts to complete the overall reaction.



The interesting question remains as to whether the reactions envisioned in mechanisms (3) and (4) are symmetry allowed. A possible molecular orbital model for the transition state is composed of a hydrogen atom complexed with the highest MO of the indenyl radical (IND·/H·). Simple LCAO calculations for the highest occupied MO of the indenyl radical,  $\psi_5$ , provide the orbital-symmetry properties pictured. This model

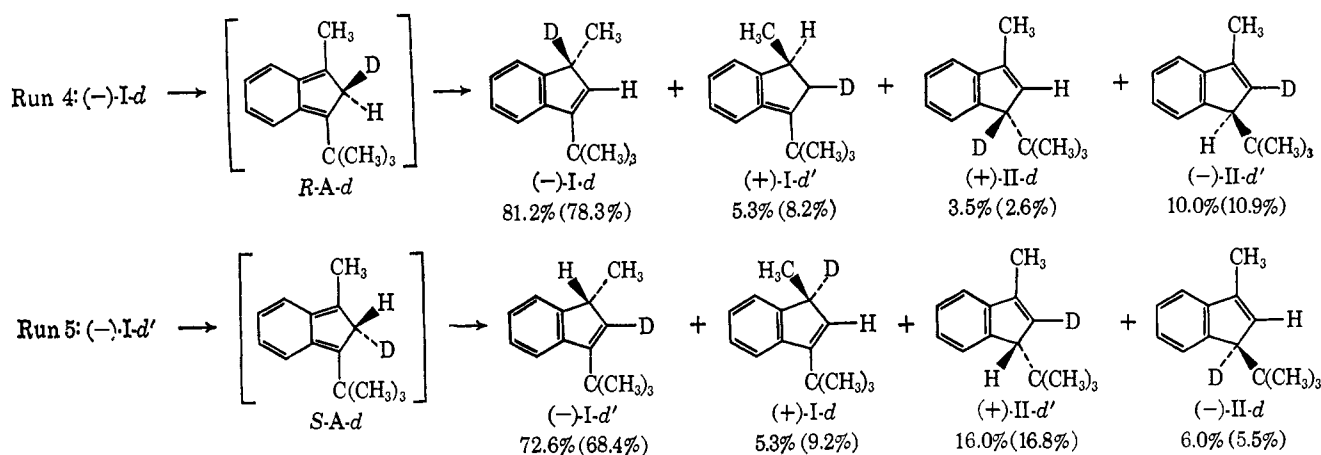
suggests that reaction sequences I → A → II, I → B, and C → II do not involve suprafacial transfer of a hydrogen atom across a nodal plane, and are symmetry allowed. This  $\psi_5$  model predicts that I → II, B → D, and B → C are orbital-symmetry disallowed for the only geometrically feasible hydrogen shift (suprafacial). However, a simpler model is available for I → A → II and I → B → C → II. For this series of 1,2-hydrogen migrations the external hexadiene  $\pi$  system is unperturbed and can be ignored,<sup>8a</sup> and the  $\pi$  system of the cyclopentadienyl radical used as a model. In this model all of the reactions of I → A → II and I → B → C → II are [1,5]-sigmatropic shifts, and the suprafacial shifts are symmetry allowed. The direct reaction, I → II, is disallowed. A still simpler model for I → II leaves the benzene ring intact,<sup>8a</sup> and involves only the  $\pi$  system of the allyl radical, whose orbital symmetry properties forbid a direct suprafacial I → II shift.<sup>8b</sup> Thus, mechanism (4) involving I → B → C → II seems the most probable explanation for the high-energy (~1%) route for isomerization.



The low-energy route for isomerization (99%) is visible in the product distribution of runs 4 and 5, and will be discussed in terms of the following assumptions. (1) The two-reaction isoindene route for I → II is the only one that needs to be taken into account. (2) Since the rotations of optically pure (–)-I-*h*, (–)-I-*d*, and (–)-I-*d'* were essentially the same, then the rotations of optically pure (–)-II-*h*, (–)-II-*d*, and (–)-II-*d'* will have the same values also. If essentially all of II produced in runs 4 and 5 passes through a substituted isoindene intermediate, then the intermediates produced from (–)-I-*d* and (–)-I-*d'* should be enantiomerically related, and should give II with the same magnitudes of rotation, but with opposite signs. The optical purity of II produced should be controlled by the kinetic isotope effect for A → II. The results of runs 4 and 5 indicate that as anticipated, the signs of rotation of II obtained were opposite. Run 4 gave (–)-II of 48% maximum rotation, whereas run 5 gave (+)-II of 42% maximum rotation. The result clearly supports the general mechanism of thermal [1,5]-sigmatropic hydrogen shifts (low-energy route). The product distributions as analyzed by glpc and polarimetric analysis for runs 4 and 5 are shown in Chart I. The positional assignments for hydrogen and deuterium were based on the configuration of intermediate A in each run. These assignments were confirmed by the product distributions calculated by glpc and nmr hydrogen-deuterium analyses, the results of which are shown in parentheses. In run 5 all product distributions have been corrected for the 7% impurity of I-*h* in the starting material.

**Isotope Effects.** Comparison of the one-point rate data for isomerization (Table I) indicates a kinetic isotope effect for the reaction I → II of about 3. This

(8) (a) R. Hoffmann, private communication; (b) R. B. Woodward and R. Hoffmann, *Angew. Chem. Intern. Ed. Engl.*, **8**, 830 (1969).

**Chart I.** Product Distributions of Runs 4 and 5, as Calculated from Glpc and Polarimetric Data of Table I<sup>a</sup>

<sup>a</sup> Calculated yields from glpc and nmr isotopic analyses are given in parentheses.

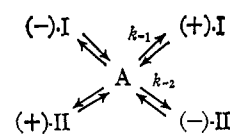
isotope effect is consistent with a transition state in which carbon-hydrogen bonds are bent much more than stretched.<sup>9</sup> The maximum  $k_h/k_d$  value based solely on the loss of one bending mode in the transition state is calculated as  $\sim 2.7$  at 25°.<sup>9d</sup>

As was anticipated earlier, the nearly identical, but opposite, rotations for II in runs 4 and 5 are the result of kinetic isotope effects for the reactions, A → II. If it is assumed that essentially all of II arises from A as an intermediate, then the kinetic isotope effect for R-A → II in run 4 and for S-A → II in run 5 can be calculated

$$\left(\frac{\%(-)\text{-II-d}'}{\%(+)\text{-II-d}}\right)_{\text{run 4}} = 2.9 \quad \left(\frac{\%(+)\text{-II-d}'}{\%(-)\text{-II-d}}\right)_{\text{run 5}} = 2.7$$

The near equality of these isotope-effect values is the result of the intermediacy of A-d, common to both reactions. The values approximate that for I → II since all the reactions involved are of similar type.<sup>10</sup>

as the collapse ratio.<sup>11</sup> The collapse ratio can be obtained directly from the amounts of (+)-I and (-)-II



benzyl H or D above  
original face of system

benzyl H or D below  
original face of system

produced from (-)-I at early stages of the reactions. If these amounts are measured at later stages, however, the product ratios alone do not accurately reflect the true collapse ratios, because much of the exchanged materials will have undergone further reactions. However, these amounts can in effect be extrapolated to zero time, and a more accurate collapse ratio determined.<sup>12</sup> This procedure has been applied to the results of runs 2, 4, and 5. Table II reports both the

**Table II.** Collapse Ratios ( $k_{(A \rightarrow I)}/k_{(A \rightarrow II)}$ ) of Isoindene Intermediates

Run no.	Starting material	Isomerization, %	Collapse ratio <sup>a,b</sup>	Corrected collapse ratios <sup>a,c</sup>		
				$k_h/k_d$ 1.0 <sup>d</sup>	$k_h/k_d$ 1.5 <sup>d</sup>	$k_h/k_d$ 3.0 <sup>d</sup>
2	(-)-I-h	43.5	0.60	1.1		
4	(-)-I-d	13.5	0.53		0.5-1.0	0.5-1.0
5	(-)-I-d'	22	1.1		1.0-1.4	1.0-1.4

<sup>a</sup> Inherent in these collapse ratios is the assumption that the collapse ratio for hydrogen migrations is the same as that for deuterium migrations. <sup>b</sup> Simply  $\% (+)\text{-I} / \% (-)\text{-II}$ . <sup>c</sup> Corrected for further reactions that (+)-I and (-)-II undergo once formed from (-)-I. <sup>d</sup> Kinetic isotope values assumed for I → II.

**Collapse Ratios.** From the data of Table I and the assumption that essentially all II passes through A as an intermediate, the relative rates at which A goes to I and II ( $k_{-1}/k_{-2}$ ) can be calculated, and will be referred to

(9) (a) M. F. Hawthorne and E. S. Lewis, *J. Amer. Chem. Soc.*, 80, 4296 (1958); (b) E. S. Lewis and M. C. R. Symons, *Quart. Rev. (London)*, 12, 230 (1958); (c) F. H. Westheimer, *Chem. Rev.*, 61, 265 (1961); (d) K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, p 351; (e) reference 7b.

(10) The differences between the values are probably due to experimental error, and cannot be attributed to the greater facility for (-)-I-d' to undergo isomerization via B and C because of an isotope effect. This possibility would give rise to different product ratios for II, but opposite in direction to those observed.

collapse ratios calculated directly from the yield data, and collapse ratios corrected for the extent of reaction. As in the former investigation,<sup>12</sup> the corrected collapse ratios are almost independent of changes in assumed

(11) The collapse ratio is used here as before<sup>9a,b</sup> in determining the preference of an intermediate to either give II or re-form I. In contrast to these previous studies which used isotopic exchange, the collapse ratio is presently determined by the relative amounts of geometric exchange in I and II. Thus, when A is formed, the relative amounts of facially inverted I and II are compared. It is important to note that  $k_{-1}/k_{-2}$  does not include an isotope effect, as the measurement is made with either hydrogen or deuterium, but not both simultaneously.

(12) D. H. Hunter and D. J. Cram, *J. Amer. Chem. Soc.*, 86, 5478 (1964).

kinetic isotope effects in the range of  $1 < k_h/k_d < 3$  which were necessary for the calculations.

The corrected collapse ratios calculated for the various runs are in rough agreement with one another, as would be expected if the reactions of A-d were not subject to secondary isotope effects. The values show that A has little, if any, preference in collapse. By contrast, in the base-catalyzed isomerization of I  $\rightarrow$  II, collapse ratios favored collapse to I by factors of 1-6, depending on the base system used.<sup>6a</sup> These results suggest that steric effects of the alkyl substituents are important when base- and solvent-bound protons are involved with an indenyl anion, but that in the thermal rearrangement these same groups have little influence on the direction of hydrogen migration in the intermediate.

### Experimental Section

(-)-2,2-Dideuterio-3-methylindanone ((-)-III-d<sub>2</sub>). To a mixture of 2.0 g of anhydrous potassium carbonate<sup>13</sup> (dried at 120° for 3 days) in 20 ml of deuterium oxide and 10 ml of dimethoxyethane (freshly distilled from lithium aluminum hydride) was added 2.0 g of 99% optically pure 3-methyl-1-indanone [ $\alpha$ ]<sup>25</sup><sub>589</sub> -16.6°, [ $\alpha$ ]<sup>25</sup><sub>546</sub> -21.9° (c 2.0, CHCl<sub>3</sub>).<sup>6a</sup> After four exchanges and work-up described previously,<sup>6a</sup> the product was flash distilled at 0.1 mm to yield 1.7 g (85% overall) of (-)-III-d<sub>2</sub>, whose nmr spectrum showed >97% exchange by comparison of integrals for the methylene and methine signals at  $\delta$  2.3 and 3.15, respectively. An ORD spectrum (c 0.015, cyclohexane) of the product was identical with that of (-)-III-d<sub>2</sub> prepared previously<sup>6a</sup> whose rotations were [ $\alpha$ ]<sup>25</sup><sub>589</sub> -16.2°, [ $\alpha$ ]<sup>25</sup><sub>546</sub> -21.4° (c 3, CHCl<sub>3</sub>).

(-)-1-Methyl-3-butylidene ((-)-I-d'). A previously described<sup>6a</sup> conversion was carried out on 1.6 g of (-)-III-d, 99% optically pure, >1.94 atom of deuterium (by nmr), to give 0.6 g (29% yield) of (-)-I-d'. Approximately 0.2 g of this material was purified by preparative glpc on a 6 ft  $\times$  1/4 in. od column packed with 10% Apiezon L on 60/80 Firebrick at 110°. The physical properties of the purified sample were as follows. Comparison of the integrals of the nmr signals for the vinyl and aromatic regions centered at  $\delta$  6.0 and 7.2 showed 93% deuteration at the vinyl position.

(13) A. C. Cope and D. M. Gale, *J. Amer. Chem. Soc.*, **85**, 3747 (1963).

The rotations of this material were: [ $\alpha$ ]<sup>25</sup><sub>589</sub> -125°, [ $\alpha$ ]<sup>25</sup><sub>546</sub> 151° (c 0.7, CHCl<sub>3</sub>). The purified material was used in run 5.

**Thermal Runs.** Pyrex tubes, 3-5 mm od, were sealed at one end, heated with chromic acid solution, then thoroughly rinsed with water, rinsed with dilute ammonia, and again with water. For runs 1, 2, 4, 5, and 6 the tubes were rinsed with dilute acetic acid before the final wash with distilled water. The tubes were dried at 130° for 8 hr prior to use. For runs 3 and 6 the tubes were not in contact with acetic acid, but were dried at 130°, rewashed exhaustively with water, and dried again for 8 hr. Omission of the water rinsings, especially after the ammonia treatment, led to dramatic rate increases in the thermal runs.

To the tubes prepared in this way were added the appropriate indene samples, whose rotations (if any) were as follows: runs 2, 3, 6, and 7, [ $\alpha$ ]<sup>25</sup><sub>589</sub> -126°, [ $\alpha$ ]<sup>25</sup><sub>546</sub> -153° (c 0.4, CHCl<sub>3</sub>); run 4, [ $\alpha$ ]<sup>25</sup><sub>589</sub> -128°, [ $\alpha$ ]<sup>25</sup><sub>546</sub> -158° (c 0.4, CHCl<sub>3</sub>); run 5, [ $\alpha$ ]<sup>25</sup><sub>589</sub> -125°, [ $\alpha$ ]<sup>25</sup><sub>546</sub> -151° (c 0.7, CHCl<sub>3</sub>). The contents were degassed four times under 0.1 mm pressure, sealed, and placed in an oil bath maintained at 140  $\pm$  2 for the appropriate period.

Procedures for the run containing the internal standard (run 1) have been described.<sup>6a</sup>

**Gas-Liquid Chromatography, Separation, Exchange, and Optical Activity Measurements on Indenes I and II.** The separation of isomers I and II was achieved on a 6 ft  $\times$  1/4 in. od column packed with 10% Apiezon on 0-80 Firebrick at 110°. The conditions of this separation have been described previously.<sup>6a</sup> Final purification, mass spectral exchange, and polarimetric analysis were made by methods described previously.<sup>6a</sup> Analysis of the per cent of hydrogen was made with a Varian A-60D instrument. Repeated (>5) integrations of the benzylic proton signal at  $\sim\delta$  3.2<sup>6c</sup> were compared with those centered at 7.2 (aromatic) and either in the region 1.0-1.5 (*t*-butyl and methyl combined) for I or at 1.0 (*t*-butyl) and 2.1 (methyl) separately for II. Since 7-15 mg of purified I or II was introduced for each analysis, uncertainty in the percentage of hydrogen at the benzyl position could be as high as  $\pm$ 30% of the figure given in Table I. Comparison of the integrals for the aromatic region of all spectra taken showed no introduction of deuterium.

**Exchange of I-d' during Preparative Gas-Liquid Chromatography.** A sample of the unpurified product I-d' (see above) was analyzed by mass spectrometry<sup>6a</sup> to have 96.8% of one atom of deuterium. After one and three purifications by preparative glpc (see above) mass spectral analysis of the compound showed 93.4 and 85.8% of deuterium, respectively. A similarly repurified sample of I-d showed no loss of deuterium or loss of optical activity.