Double-Bond Rearrangements of Inden-1-yl Derivatives

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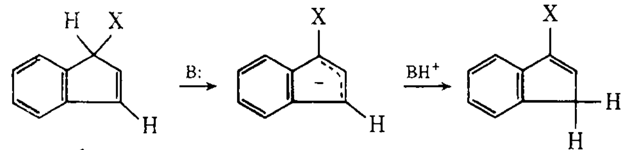
Received September 18, 1974

The rates of double-bond rearrangement of ten different inden-1-yl derivatives to the corresponding inden-3-yl derivatives have been determined in pyridine at 40°. No linear free-energy relationship has been found which fits all of the data. However, the unexpectedly high reactivities observed for many of the compounds clearly indicate the care with which they must be handled in the presence of even weakly basic amines if their isomeric integrities are to be preserved.

In connection with another investigation, we have carried out a study of the rates of pyridine promoted double-bond rearrangement of a variety of inden-1-yl derivatives **1** to the corresponding inden-3-yl derivatives **2**. Such amine promoted rearrangements are well documented in the literature,[1-4] and have recently received considerable attention due to the fact that they have been shown[2] to proceed *via* a suprafacial conducted tour route for the 1,3-proton transfer. However, except for 1-deuterioindene[3] and various alkyl-substituted indenes,[2,4] only very qualitative kinetic data are available and most of these have been obtained using a wide variety of bases, solvents, and reaction conditions.



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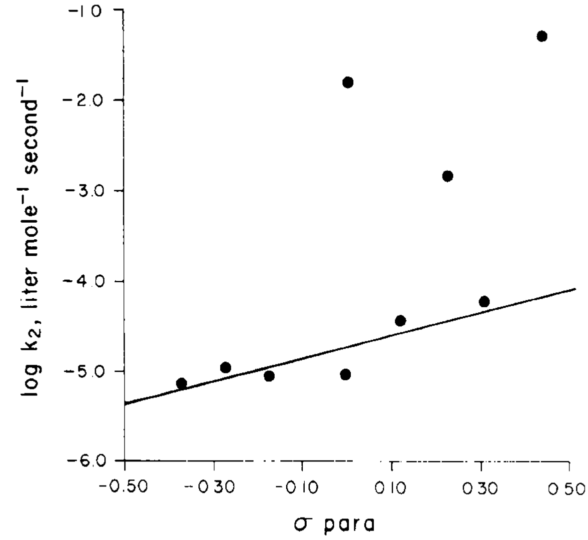

Figure 1. Plot of log k_2 *vs.* σ para for rearrangement of inden-1-yl derivatives in pyridine at 39.5 ± 1.5°.

For our kinetic studies, small scale nmr techniques were used to follow the course of the rearrangements. Pyridine was used simultaneously as the base and the solvent, and all of the rearrangements were examined at 39.5 ± 1.5°. The inden-1-yl derivatives examined were limited to those which were already available to us in connection with our other investigation, or which could be readily synthesized from these. However, the substituents present on these derivatives represent a variety of inductive and resonance effect behaviors. The syntheses and characterizations of each of the inden-1-yl and -3-yl derivatives encountered are described in the Experimental Section. Five of the inden-1-yl derivatives are reported here for the first time.

In all of the cases we have examined, the rearrangements of the inden-1-yl derivatives proceeded cleanly to the corresponding inden-3-yl derivatives or an equilibrium mixture, except for inden-1-ol which gave indan-1-one *via* enol–keto tautomerization of the initially formed inden-3-ol. The kinetic data obtained for the rearrangements are summarized in Table I. The average integrated first-order rate constants given for the forward processes in the rearrangements studied were calculated assuming that pseudo-first-order or reversible pseudo-first-order rate behavior would be followed.[5]

For most of the rearrangements which proceeded at convenient rates the correctness of this assumption was borne out by the fits obtained for the data. The errors shown are mean deviations of the integrated first-order rate constants calculated from at least six or seven experimental points. However, the pseudo-first-order reversible fit for the data from rearrangement of 3-deuterioindene was very poor owing to the experimental inaccuracies inherent in the fact that the rearrangement was followed by integration of an nmr absorption which only decreased by 30% overall during the course of the rearrangement. Thus, the data were treated graphically. In the case of 1-phenylindene, the rearrangement was so fast that the earliest point which could be measured indicated over 58% rearrangement and the rate constant shown is the best estimate available from several runs. Finally, for the inden-1-yl carboxylic acid, in all cases by the time an nmr spectrum of the reaction mixture could be taken only the presence of the inden-3-yl derivative could be observed. Thus, the rate constant given in this case is only a minimum value.

Table I also gives the values for the calculated second-order rate constants for the rearrangements studied. No error is given for these since they include the errors in pyridine concentrations. These errors in concentration may be as great as ±5% owing to the problems inherent in measuring the very small volumes of the reaction mixtures used.

It is seen that for the inden-1-yl derivatives examined the rates for rearrangement spanned a range of at least four powers of ten. The high reactivities for even the acetate, *p*-nitrobenzoate, and 3,5-dinitrobenzoate derivatives clearly point out the care with which an experimentalist must handle inden-1-yl derivatives even in the presence of weak bases such as pyridine if problems due to isomerization to the corresponding inden-3-yl derivatives are not to be encountered.

Attempts to find a linear free-energy relationship which would give a good fit for all of the data were unsuccessful, as might have been expected and as is shown by the σ para plot given in Figure 1. Various other treatments involving use of different types of σ values in the Hammett relation-

Table I
Rates of Double-Bond Rearrangement of Some Inden-1-yl Derivatives in Pyridine at 39.5 ± 1.5°

Substituent	[Indene], M	[Pyridine], M	% conversion at equilibrium	$10^4 k_1$, sec^{-1}	$10^5 k_2$, M^{-1} sec^{-1} [a]
$-OH$	3.6	6.7	99 ± 1[b]	0.050 ± 0.001	0.075
	3.3	7.2	99 ± 1[b]	0.052 ± 0.002	0.072
	3.3	7.2	99 ± 1[b]	0.051 ± 0.004	0.071
$-CH_3$	3.7	6.5	97 ± 2	0.053 ± 0.002	0.082
	3.5	6.9	99 ± 1[c]	0.053 ± 0.002	0.077
	3.3	7.1	99 ± 1[c]	0.074 ± 0.004	0.10
$-H$[d]	3.9	6.9	63 ± 5	0.059[e]	0.086
	3.2	8.0	60 ± 5	0.068[e]	0.085
$-OCH_3$	3.0	7.1	94 ± 2	0.080 ± 0.010	0.11
	2.7	7.9	94 ± 2	0.074 ± 0.008	0.094
	3.3	6.6	91 ± 2	0.074 ± 0.008	0.11
$-CH_2OH$	3.6	6.1	94 ± 1	0.22 ± 0.01	0.36
	3.4	6.4	94 ± 1	0.23 ± 0.02	0.36
	3.3	6.6	94 ± 1	0.19 ± 0.01	0.29
	2.8	7.5	91 ± 1	0.22 ± 0.01	0.29
$-OAc$	2.4	7.4	96 ± 1	0.39 ± 0.01	0.53
	2.3	7.6	97 ± 1	0.43 ± 0.03	0.57
	2.7	6.8	96 ± 1	0.34 ± 0.03	0.50
	2.5	7.2	96 ± 1	0.40 ± 0.02	0.56
$-OPNB$	1.1	8.8	95 ± 5	1.8 ± 0.1	2.0
	1.2	8.3	95 ± 5	1.4 ± 0.1	1.7
$-ODNB$	0.61	10	95 ± 5	3.5 ± 0.2	3.5
	0.59	10	95 ± 5	4.5 ± 0.1	4.5
$-Cl$	2.3	8.3	99 ± 1[c]	12 ± 1	14
	2.4	8.2	99 ± 1[c]	8.6 ± 1	10
	2.2	9.0	99 ± 1[c]	14 ± 1	16
$-C_6H_5$	1.8	8.2	99 ± 1[c]	120[f]	150
$-CO_2H$	1.6	9.5	99 ± 1[c]	> 460	> 480

[a] 10^4k_1 divided by [pyridine]. [b] No starting material observed under conditions where 1% would have been clearly observed. [c] Less than 1% starting material observed. [d] Starting material is 3-deuterioindene. [e] Determined graphically. [f] Determined graphically with points from several different runs being plotted together.

ship as well as steric effects were also considered and gave even poorer fits. That a simple Hammett type correlation for the 1-substituted indene isomerization data should not be expected is apparent from consideration of several factors. The rate constants we measured are for formation of isomerized product and not for proton abstraction at the 1 position. These should not be identical with varying 1 substituents owing to the likelihood of invisible proton readdition to the 1 position, and also would not be expected to have a constant ratio. Furthermore, not only inductive and conjugative effects but also the differing steric and dipolar field effect interactions of the 1 substituents should greatly affect the stabilities of the respective activated complexes for 1-proton abstraction.

For completeness, we have also made a brief examination of the literature for evidence regarding the propensities for rearrangement of our and other inden-1-yl to inden-3-yl derivatives in the presence of bases. A number of examples of the rearrangements of 1-alkylindenes are available in the literature, as mentioned earlier. In accord with the high reactivity we observed for 1-phenylindene, Kende and Bogard[6] reported that this material in deuteriochloroform solution at room temperature rapidly isomerized to 3-phenylindene upon the addition of one drop of triethylamine. Also, Meth-Cohn and Gronowitz[7] reported the instantaneous rearrangement of inden-1-yl carboxylic acid upon similar treatment. Finally, Kerber and Hodos[8] observed that 1-nitroindene was rapidly isomerized to 3-nitroindene in deuteriochloroform solution at room temperature even in the absence of added base.

Experimental Section

Melting points and boiling points are uncorrected. Nmr spectra were obtained on a Varian A-60A instrument with chemical shifts measured in parts per million (δ) downfield from TMS internal or external standard. Mass spectra were run on a CEC Model 21-104 single focusing instrument by Mr. J. Voth. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Indan-1-one. This was prepared in 62% yield by the procedure of Arcus and Barrett[9] through the reaction of hydrocinnamic acid (Eastman White Label) and polyphosphoric acid: bp 89–90° (0.6 mm); mp 39–40° [lit.[9] bp 120–122° (15 mm); mp 38°]; nmr (CCl_4) δ 2.5 (m, 2 H, $C\mathbf{H}_2C{=}O$), 2.9 (m, 2 H, $C\mathbf{H}_2$-arom), and 7.4 ppm (m, 4 H, **arom**).

1-Deuterioindan-1-ol. This was prepared on small scale in 50% yield by reduction of indan-1-one with lithium aluminum deuteride (Ventron, 18.7% D) and recrystallized from 1:1 ether–petroleum ether: mp 51–53° [lit.[10] mp 53–54° (for nondeuterated material)]; nmr (CCl_4) δ 2.0 (m, 2 H, $C\mathbf{H}_2CDOH$), 2.7 (m, 2 H, $C\mathbf{H}_2$-arom), 4.3 (bs, 1 H, $O\mathbf{H}$), and 7.1 ppm (m, 4 H, **arom**). Nmr examination showed that this material contained less than 2% of one H on C_1 (δ 4.9 ppm).

3-Deuterioindene. A finely crushed mixture of 1.0 g (0.0074 mol) of 1-deuterioindan-1-ol and 1.3 g (0.011 mol) of anhydrous magnesium sulfate when heated to 120° at 32 mm pressure yielded 0.6 g (69%) of crude product. Redistillation through a microdistillation apparatus gave 0.5 g of pure 3-deuterioindene: bp 85–88° (35 mm); $n^{23.5}D$ 1.5740 [lit.[11] bp 182 (740 mm); $n^{25}D$ 1.5739 (for nondeuterated material)]; nmr (CCl_4) δ 3.2 (d, J = 2 Hz, 2 H, CH-$C\mathbf{H}_2$), 6.3 (m, 1 H, $={C\mathbf{H}}$-CH_2) and 7.1 ppm (m, 4 H, **arom**); mass spectrum (70 eV) m/e (rel intensity) 118 (10), 117 (100), 116 (81), 115 (14), 63 (11), 58 (9), 39 (8). Nmr examination showed that this material contained less than 2% of one H on C_3 (δ 6.6 ppm).

Inden-1-ol. This was prepared in 33% overall yield by a modified method from that of Hock and Ernst.[12] Oxygenation of inden-

1-yllithium at −78° followed by reduction of the intermediate inden-1-yl hydroperoxide with potassium iodide in aqueous acetic acid produced the desired inden-1-ol; bp 95–96° (1.4 mm). It was recrystallized from 4:1 petroleum ether–ether to yield white plates: mp 55–56° (lit.[13] mp 47°); nmr (CCl_4) δ 3.2 (bs, 1 H, CHO**H**), 4.9 (bs, 1 H, C**H**OH), 6.2 (doublet of doublets, *J* = 2 and 6 Hz, 1 H, C**H**-CHOH), 6.5 (doublet of doublets, *J* = 1 and 6 Hz, 1 H, **CH**-arom), and 7.3 ppm (m, 4 H, **arom**); mass spectrum (70 eV) *m/e* (rel intensity) 132 (100), 131 (79), 115 (15), 104 (15), 103 (34), 77 (34), 51 (30), 50 (10), and 18 (20).

3-Methylindan-1-one. This was prepared in 82% yield by the method of Koelsch and coworkers[13] through the reaction of crotonic acid with benzene in the presence of aluminum chloride: bp 78–85° (1.5 mm); n^{24}D 1.5555 [lit.[13] bp 132–137° (15 mm)]; nmr (CCl_4) δ 1.3 (d, *J* = 7 Hz, 3 H, **CH**$_3$), 2.2 (doublet of doublets, *J* = 4 and 19 Hz, 1 H, C**H**-C=O), 2.7 (doublet of doublets, *J* = 7 and 19 Hz, 1 H, C**H**-C=O), 3.3 (m, 1 H, C**H**-CH_3), and 7.4 ppm (m, 4 H, **arom**).

3-Methylindan-1-ol. Reduction of 3-methylindan-1-one in ether with lithium aluminum hydride followed by recrystallization from petroleum ether gave a 61% yield of 3-methylindan-1-ol as *tiny white needles: mp 70–72° (lit.[15] mp 69°); nmr (CCl_4) δ 1.3 (m,* 4 H, CH-**CH**$_3$), 2.8 (m, 2 H, **CH**$_2$), 4.5 (bs, 1 H, **OH**), 5.2 (t, *J* = 8 Hz, 1 H, **CH**-OH), and 7.5 ppm (m, 4 H, **arom**).

1-Methylindene. This was prepared on small scale in 31% yield by the method of Bergson and Weidler[4a] through 20% sulfuric acid catalyzed dehydration of 3-methylindan-1-ol at 100°; bp 64–70° (10 mm); $n^{23.5}$D 1.5554 [lit.[14] bp 82° (15 mm); n^{20}D 1.5569]; nmr (CCl_4) δ 1.3 (d, *J* = 7 Hz, 3 H, **CH**$_3$), 3.4 (q, *J* = 7 Hz, 1 H, **CH**-CH_3), 6.4 (doublet of doublets, *J* = 2 and 6 Hz, 1 H, =**CH**-CH), 6.7 (doublet of doublets, *J* = 2 and 6 Hz, 1 H, = **CH**-arom), and 7.2 ppm (m, 4 H, **arom**).

In another preparation, 67.3 g (0.46 mol) of 3-methylindan-1-ol and 90 g (0.75 mol) of powdered anhydrous magnesium sulfate were heated at 140–155° for about 1 hr (18 mm). The dried distillate consisting of 1-methylindene weighed 53 g (88%).

3-Methylindene. 1-Methylindene (53 g, 0.41 mol) was refluxed with 5 ml of triethylamine for 2 hr. Distillation afforded 50 g (94%) of 3-methylindene: bp 77–79° (18 mm); n^{21}D 1.5565 [lit.[15] bp 70° (10 mm); n^{25}D 1.5595]; nmr (Et_3N) δ 1.8 (m, 3 H, **CH**$_3$), 2.8 (m, 2 H, **CH**$_2$-arom), 5.7 (m, 1 H, =**CH**-CH_2), and 6.9 ppm (m, 4 H, **arom**).

1-Methoxyindene. Into a 100-ml flask was added 2.0 g (0.015 mol) of inden-1-ol and 20 ml of trimethyl orthoformate. Then 3.2 g (0.032 mol) of 70% aqueous perchloric acid was added dropwise. The solution was stirred for 20 min at *ca.* 35° and then was poured into 100 ml of ice-cold saturated aqueous sodium bicarbonate. The resulting mixture was extracted with three 30-ml portions of ether. The combined ether extracts were washed with saturated aqueous sodium chloride, dried over anhydrous sodium sulfate, and concentrated by rotary vacuum evaporation. Distillation of the remaining oil afforded 1.1 g (50%) of 1-methoxyindene: bp 71–74° (3.9 mm); $n^{23.5}$D 1.5531; nmr (CCl_4) δ 3.1 (s, 3 H, O**CH**$_3$), 5.0 (bs, 1 H, **CH**-OCH_3), 6.4 (doublet of doublets, *J* = 2 and 4 Hz, 1 H, =**CH**-CH-OCH_3), 6.8 (d, *J* = 6 Hz, 1 H, =**CH**-arom), and 7.2 ppm (m, 4 H, **arom**); mass spectrum (70 eV) *m/e* (rel intensity) 147 (11), 146 (100), 145 (11), 131 (88), 115 (64), 103 (91), 77 (30), and 63 (29).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.04; H, 6.87.

3-Methoxyindene. 1-Methoxyindene (0.23 g, 0.0016 mol) was heated with 0.3 ml of triethylamine at 40° for 1 hr. Distillation yielded 0.17 g (74%) of 3-methoxyindene contaminated with 4% of 1-methoxyindene: bp 116–117° (20 mm); $n^{23.5}$D 1.5657 [lit.[16] bp 101–104° (15 mm)]; nmr (CCl_4) δ 3.2 (d, *J* = 2 Hz, 2 H, **CH**$_2$-arom), 3.8 (s, 3 H, O**CH**$_3$), 5.1 (t, *J* = 2 Hz, 1 H, **CH**=CH-OMe), and 7.2 ppm (m, 4 H, **arom**).

1-Hydroxymethylindene. This was material containing 5% 3-hydroxymethylindene prepared by Friedrich and Holmstead[17] by the reaction of indenylmagnesium bromide with paraformaldehyde: bp 88–91° (0.8 mm) [lit.[18] bp 134° (10 mm)]; nmr (CCl_4) δ 3.6 (m, 4 H, **HOCH**$_2$**CH**), 6.4 (d, 1 H, *J* = 5 Hz, =**CH**-$CHCH_2OH$), 6.7 (d, 1 H, *J* = 5 Hz, =**CH**-arom) and 7.1 ppm (m, 4 H, **arom**).

3-Hydroxymethylindene. A mixture of 5.0 g (0.034 mol) of 1-hydroxymethylindene and 2 ml of cyclohexylamine in 20 ml of ether was refluxed for 10 min. The resulting mixture was washed with 5 ml of 1 *M* hydrochloric acid, dried over anhydrous magnesium sulfate, and distilled at 100–108° (1.2 mm) to produce 2.6 g (52%) of crude 3-hydroxymethylindene. Recrystallization from 20 ml of 1:1 chloroform–carbon tetrachloride afforded 2.0 g of white crystals: mp 67–69° (lit.[19] mp 68°); nmr ($CDCl_3$) δ 2.9 (bs, 1 H, **OH**), 3.2 (m, 2 H, **CH**$_2$), 4.5 (m, 2 H, **CH**$_2$OH), 6.4 (m, 1 H, =**CH**-CH_2), and 7.3 ppm (m, 4 H, **arom**).

1-Acetoxyindene. A mixture of 0.74 g (0.0056 mol) of inden-1-ol and 3 ml (0.042 mol) of acetyl chloride was refluxed on a steam bath for 10 min. Distillation yielded 0.71 g (73%) of 1-acetoxyindene: bp *ca.* 85° (1 mm); n^{24}D 1.5455; nmr (CCl_4) δ 2.0 (s, 3 H, **CH**$_3$), 6.2 (m, 2 H, =**CH**-**CH**-OAc), 6.6 (d, *J* = 5 Hz, 1 H, =**CH**-arom), and 7.2 ppm (m, 4 H, **arom**).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.84; H, 5.93.

3-Acetoxyindene. A mixture of 0.42 g (2.4 mmol) of 1-acetoxyindene and 0.5 ml of triethylamine was heated at 40° for 1.5 hr. Distillation produced 0.19 g (45%) of a 95:5 mixture of the 3- and 1-acetoxyindenes: bp 78–81° (0.6 mm); $n^{23.5}$D 1.5512 [lit.[20] bp 77–85° (0.2–0.25 mm)]; nmr (CCl_4) δ 2.1 (s, 3 H, **CH**$_3$), 3.2 (d, *J* = 2 Hz, 2 H, **CH**$_2$), 6.3 (m, 1 H, =**CH**-CH_2), and 7.2 ppm (m, 4 H, **arom**).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.68; H, 5.66.

Inden-1-yl *p*-Nitrobenzoate. A mixture of 1.0 g (0.0076 mol) of inden-1-ol and 1.5 g (0.0081 mol) of recrystallized *p*-nitrobenzoyl chloride in 20 ml of pyridine at −15° was stirred intermittently *over a period of* 1.5 hr. The mixture was poured into 100 ml of 1 *M* hydrochloric acid and the precipitate collected was recrystallized from 2:1 pentane–chloroform to afford 1.05 g (48%) of the desired *p*-nitrobenzoate: mp 81–83°; nmr ($CDCl_3$) δ 6.5 (m, 2 H, =**CH**-**CH**OPNB), 6.9 (m, 1 H =**CH**-arom), 7.3 (m, 4 H, **arom**), and 8.2 ppm (m, 4 H, **arom**).

Anal. Calcd for $C_{16}H_{11}NO_4$: C, 68.36; H, 3.94. Found: C, 68.59; H, 3.96.

Inden-3-yl *p*-Nitrobenzoate. A mixture of 0.6 g (0.0021 mol) of inden-1-yl *p*-nitrobenzoate and 0.5 ml of triethylamine in 10 ml of chloroform was refluxed for 20 min. Removal of the solvent gave a solid which was recrystallized from 10 ml of 1:1 chloroform–petroleum ether to afford 0.4 g (67%) of inden-3-yl *p*-nitrobenzoate: mp 122–124° [lit.[12] mp 122°]; nmr ($CDCl_3$) δ 3.4 (d, *J* = 2 Hz, 2 H, CH_2), 6.5 (t, *J* = 2 Hz, 1 H, =**CH**-CH_2), 7.3 (m, 4 H, **arom**), and 8.2 ppm (m, 3 H, **arom**).

Inden-1-yl 3,5-Dinitrobenzoate. A sample of 30 ml of pyridine was cooled to −25°, and 1.7 g (0.013 mol) of inden-1-ol was added followed in portions by 3.5 g (0.015 mol) of 3,5-dinitrobenzoyl chloride. The mixture was kept at −20 to −25° for 2 hr and then poured into 150 ml of ice-cold 0.3 *M* HCl. The precipitate was collected and recrystallized from 150 ml of 1:1 chloroform–petroleum ether to yield 2.55 g of powdery beads, mp 142–145°, and 0.80 g, mp 136–141°. The overall yield was 86% and the material showed no inden-3-yl rearrangement product: nmr ($CDCl_3$) 6.5 (1 H, CH-CH-ODNB), 6.5 (bs, 1 H, CH-ODNB), 6.9 (dd, *J* = 2 and 6 Hz, 1 H, CH-arom), 7.3 (m, 4 H, **arom**), and 9.2 ppm (s, 3 H, **arom**).

Anal. Calcd for $C_{16}H_{10}N_2O_4$: C, 58.90; H, 3.09; N, 8.59. Found: C, 58.76; H, 3.13; N, 8.42.

Inden-3-yl 3,5-Dinitrobenzoate. *Into a well stirred solution of* 30 ml of pyridine and 1 g (0.0082 mol) of inden-1-ol at room temperature was added in portions 2.2 g (0.092 mol) of 3,5-dinitrobenzoyl chloride. After standing for 1 hr at room temperature, the solution was poured into ice–water and the precipitate collected was recrystallized from 1:1 chloroform–methylcyclohexane to give 0.7 g (35%) of inden-3-yl 3,5-dinitrobenzoate: mp 179–182° (lit.[12] 181°); nmr ($CDCl_3$) δ 3.6 (d, *J* = 2 Hz, 2 H, **CH**$_2$), 6.7 (t, *J* = 2 Hz, 1 H, =**CH**-CH_2), 7.5 (m, 4 H, **arom**) and 9.4 ppm (m, 3 H, **arom**).

Anal. Calcd for $C_{16}H_{10}N_2O_4$: C, 58.90; H, 3.09; N, 8.59. Found: C, 58.71; H, 3.26; N, 8.42.

Also obtained as a second crop from the recrystallization was 0.7 g of a mixture of the inden-1-yl and -3-yl 3,5-dinitrobenzoates, mp 131–140°.

1-Chloroindene. A mixture of 1.25 g (0.0095 mol) of inden-1-ol and 6 ml (0.083 mol) of thionyl chloride was refluxed for 30 min. Distillation of the reaction mixture produced 0.65 g (46%) of 1-chloroindene: bp 68–71° (2.7 mm); n^{24}D 1.5865; nmr (CCl_4) δ 5.1 (s, 1 H, CHCl), 6.2 (doublet of doublets, *J* = 2 and 6 Hz, 1 H, =CH-CHCl), 6.6 (d, *J* = 6 Hz, 1 H, =CH-arom), and 7.1 ppm (m, 4 H, **arom**).

Anal. Calcd for C_9H_7Cl: C, 71.78; H, 4.68. Found: C, 71.66; H, 4.65.

3-Chloroindene. A mixture of 0.65 g of 1-chloroindene and 2 ml of triethylamine was refluxed for a short period and then distilled to yield 0.35 g (54%) of 3-chloroindene: bp 78–81° (4 mm); n^{24}D 1.5817 [lit.[21] bp 109–110° (16 mm); n^{23}D 1.5808]; nmr (neat) δ 2.9 (d, *J* = 2 Hz, 2 H, **CH**$_2$-arom), 6.1 (t, *J* = 2 Hz, 1 H, **CH**=C-Cl), and 7.2 ppm (m, 4 H, **arom**).

3-Phenylindan-1-one. This was prepared in 40% yield by the procedure of Baker[22] and coworkers involving the reaction of

Table II
Chemical Shifts and Assignments of the Nmr Absorptions Integrated during the Rearrangement Studies

Substituent	Inden-1-yl derivative	Product	Internal standard
$-OH$	5.1 (bs, CHOH)	2.0 (m, $C\mathbf{H}_2C{=}O$) and 2.4 (m, CH_2-arom)[a]	D[b]
$-CH_3$	0.8 (d, $C\mathbf{H}_3$)	1.4 (m, CH_3)	H[c]
$-H$	2.5 (d, CH_2)	2.5 (d, $C\mathbf{H}_2$)[d]	H
$-OCH_3$	2.7 (s, OCH_3)	3.2 (s, CH_3)	H
$-CH_2OH$	3.4 (m, $CHCH_2OH$)	3.2 (m, CH_2-arom) and 4.4 (m, CH_2OH)	D
$-OAc$	1.5 (s, O-C(O)CH_3)	1.7 (s, O-C(O)CH_3)	D
$-OPNB$	*e*	2.8 (d, CH_2)	H
$-ODNB$	*e*	2.8 (d, CH_2)	H
$-Cl$	4.7 (bs, CHCl)	2.6 (d, CH_2)	H
$-Ph$	4.6 (CHC_6H_5)	2.2 (d, CH_2)	H
$-CO_2H$	*f*	2.8 (bs, CH_2)	H

[a] Final product is indan-1-one. [b] Cyclododecane 0.7 (s, CH_2). [c] Cyclohexane 0.8 (s, CH_2). [d] The rearrangement product is 1-deuterioindene. [e] It was not possible to successfully integrate any protons of the starting material due to their close proximity to the pyridine solvent. [f] Unable to observe the α proton of indene-1-carboxylic acid because of the rapid rearrangement in pyridine.

trans-cinnamic acid with benzene in the presence of aluminum chloride followed by recrystallization from 2:1 petroleum ether–ether: mp 77–78° [lit.[22] mp 78°]; nmr (CCl_4) 2.6 (q, J = 4 and 19 Hz, 1 H, CH_2), 3.0 (q, J = 8 and 19 Hz, 1 H, CH_2), 4.5 (q, J = 4 and 8 Hz, 1 H, CH-CH_2), and 7.2 ppm (m, 9 H, **arom**).

3-Phenylindan-1-ol. A crude sample of this material was prepared in 88% yield by the reduction of 3-phenylindan-1-one with lithium aluminum hydride in ether: mp 75–88° (lit.[23] 95°); nmr (CCl_4) δ 1.8 (m, 1 H, CH_2) 2.8 (m, 1 H, CH_2), 3.0 (m, 1 H, OH), 3.9 (t, J = 8 Hz, 1 H, CH-C_6H_5), 5.0 (t, J = 8 Hz, 1 H, CHOH), and 7.0 ppm (m, 9 H, **arom**).

1-Phenylindene. This was prepared in 82% yield following the method of Marechal and Hamy[24] *via* heating 3-phenylindan-1-ol with anhydrous magnesium sulfate at 160° (0.9 mm): bp 111–114° (0.9 mm); nmr (CCl_4) δ 4.1 (m, 1 H, CH-C_6H_5), 6.1 (doublet of doublets, J = 2 and 6 Hz, 1 H, $=CH$-CH-C_6H_5), 6.4 (doublet of doublets, J = 2 and 6 Hz, 1 H, CH-arom), and 6.7 ppm (m, 9 H, **arom**).

3-Phenylindene. A mixture of 1-phenylindene and 3-phenylindene (0.6 g, 0.0031 mol) was mixed with 0.2 ml of triethylamine and distilled to yield 0.35 g (58%) of 3-phenylindene: bp 117–119° (0.3 mm) [lit.[25] bp 113–116° (0.4 mm)]; nmr (CCl_4) δ 3.4 (d, J = 2 Hz, 2 H, CH_2), 6.7 (t, J = 2 Hz, 1 H, $=CH$-CH_2), and 7.7 ppm (m, 9 H, **arom**).

Indene-1- and -3-carboxylic Acids. A solution of phenyllithium in 170 ml of ether was prepared by the reaction of 0.99 g (0.142 mol) of metallic lithium and 11.2 g (0.071 mol) of bromobenzene. Then 8.5 g (0.073 mol) of indene in 25 ml of ether was added dropwise, and the solution was stirred for 15 min at room temperature, cooled to −78°, and poured rapidly into 300 g of freshly crushed solid carbon dioxide. The resulting slurry was stirred briefly and then poured into 300 ml of rapidly stirred 10% aqueous hydrochloric acid at 0°. Work-up and recrystallization from 30–60° petroleum ether afforded 2.2 g (23%) of a mixture consisting mainly of the indene-1-carboxylic acid as cream colored crystals: mp 73–77° (lit.[8] mp 73–74°); nmr ($CDCl_3$) δ 4.6 (bs, 1 H, CH-CO_2H), 6.8 (doublet of doublets, J = 6 and 2 Hz, 1 H, $=CH$-arom), 7.1 (doublet of doublets, J = 6 and 2 Hz, 1 H, $CH{=}CH$-arom), 7.6 (m, 4 H, **arom**), and 11.9 ppm (s, 1 H, $CO_2\mathbf{H}$). There was also obtained 5.3 g (55%) of indene-3-carboxylic acid as orange needles: mp 158–161° (lit.[26] mp 158–159°); nmr ($CDCl_3$) δ 3.5 (d, J = 2 Hz, 2 H, CH_2), 7.4 (m, 3 H, **arom**), 7.6 (t, J = 2 Hz, 1 H, $=CH$-CH_2), 8.1 (m, 1 H, **arom**), and 11.4 ppm (bs, 1 H, $CO_2\mathbf{H}$).

Procedure for Rearrangement Studies. In the usual procedure where the rates of rearrangement were not too rapid (acetoxy or slower) or the substituted indene did not present solubility problems, *ca.* 0.2 g of the substituted indene, *ca.* 0.3 g of pyridine (redistilled from CaH_2), and *ca.* 20 mg of cyclododecane internal standard were carefully weighed using an analytical balance into an nmr tube. The tube was swept with nitrogen and sealed, and the contents were mixed well. The tube was then placed into a constant temperature oil bath at 40.7 ± 0.2° and the appropriate regions of the nmr spectrum were integrated at six or seven convenient intervals during the course of the rearrangement. An infinity point was measured after approximately 10 half-lives for rearrangement. The chemical shifts in pyridine and assignments of the absorptions in the nmr spectra which were integrated for each of the internal standards, inden-1-yl and inden-3-yl derivatives, for the purposes of following the rearrangements are given in Table II. These chemical shifts are only approximate since they varied slightly with concentration from run to run. In cases where the rearrangements were slow, several integrations of each region were taken for high accuracy. However, in cases where the rearrangements were fast only one integration of each region was taken. Where the rates of rearrangement were very fast, the tube was left in the probe during the entire run. For the purposes of rate constant calculations, the times during which the tube was in the probe (temperature 39.5 ± 1.5°) in all cases were included in the rearrangement times. In representative cases after a run was completed, the volume of the reaction mixture, needed for calculation of second-order rate constants, was measured by determining the weight of an equal volume of water. From these volume measurements, it was found that the densities of all of the various solutions were 1 g/ml within about 5% deviation. Thus, for all of the concentration calculations reported in Table I the volume in milliliters of the reaction mixture was taken as equivalent to its weight in grams.

Acknowledgment. We wish to thank the Committee on Research of the University of California, Davis for partial support of this study.

Registry No.—Indan-1-one, 83-33-0; 1-deuterioindan-1-ol, 53820-82-9; 3-deuterioindene, 933-61-9; inden-1-ol, 53820-83-0; 3-methylindan-1-one, 6072-57-7; 3-methylindan-1-ol, 22339-44-2; 1-methylindene, 767-60-2, 3-methylindene, 767-59-9; 1-methoxyindene, 27973-23-5; trimethyl orthoformate, 149-73-5; 3-methoxyindene, 53820-84-1; 1-hydroxymethylindene, 2471-87-6; 3-hydroxymethylindene, 2471-88-7; 1-acetoxyindene, 19455-83-5; 3-acetoxyindene, 35116-20-2; inden-1-yl *p*-nitrobenzoate, 53820-85-2; *p*-nitrobenzoyl chloride, 122-04-3; inden-3-yl *p*-nitrobenzoate, 53820-86-3; inden-1-yl 3,5-dinitrobenzoate, 53820-87-4; 3,5-dinitrobenzoyl chloride, 99-33-2; inden-3-yl 3,5-dinitrobenzoate, 53820-88-5; 1-chloroindene, 25894-22-8; 3-chloroindene, 53820-89-6; 3-phenylindan-1-one, 16618-72-7; 3-phenylindan-1-ol, 30516-40-6; 1-phenylindene, 1961-97-3; 3-phenylindene, 1961-96-2; indene-1-carboxylic acid, 14209-41-7; indene-3-carboxylic acid, 5020213.

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