

Table VI. ORD Data for Irradiated and Unirradiated (+)-1,2-Dimethylindene<sup>a</sup>

$\lambda$ , nm	unirradiated		irradiated		% drop <sup>c</sup>
	$\alpha^\circ$	$[\alpha]_\lambda^{27}$ <sup>b</sup>	$\alpha^\circ$	$[\alpha]_\lambda^{27}$	
395	0.0838	286.7	0.0874	287.0	-0.10
365	0.1093	373.9	0.1145	376.0	-0.56
355	0.1202	411.2	0.1250	410.5	0.17
350	0.1265	432.8	0.1321	433.8	-0.23
340	0.1403	480.0	0.1460	479.5	0.10
330	0.1574	538.5	0.1641	538.9	-0.07
320	0.1792	613.1	0.1861	611.2	0.31
310	0.2079	711.3	0.2146	704.8	0.91
305	0.2287	782.4	0.2386	783.6	-0.15
325	0.1661	568.3	0.1740	571.4	-0.55
345	0.1332	455.7	0.1395	458.1	-0.53
335	0.1487	508.7	0.1548	508.4	0.06
296	0.3850	1313	0.3953	1298	1.44

<sup>a</sup> Instrument sensitivity  $-0.4^\circ$  full scale. <sup>b</sup>  $[\alpha]_\lambda^T = \alpha/dc$  where  $d = 0.100$  dm and  $c =$  concentration in grams per milliliter. <sup>c</sup> Average 0.06, standard deviation 0.58.

mixtures or by analyzing isolated 1,2-dimethylindene. An example of the latter is described below: a solution of 60 mg of the indene in 50 mL of hexane was added to a Vycor tube, argon degassed, and photolyzed with the Hanovia low-pressure lamp for 68 min.

VPC analysis on column D at 100 °C indicated 9.97% conversion to 2,3-dimethylindene. The 1,2-dimethylindene was isolated by using column H; 30.45 mg of the recovered material was diluted to 10.00 mL with hexane and analyzed by ORD. The data are presented in Table VI.

**Acknowledgment.** We are grateful to Dr. B. Bigot for helpful discussions of the correlation diagrams, Professor W. Jorgensen for providing the extended Hückel program, and Professor F. Lytle for assistance in the design of the singlet lifetime instrument. Partial financial support from the Purdue Research Foundation, Standard Oil of Ohio, and the U.S. Army Research Office is gratefully acknowledged.

**Registry No.** 1, 63265-70-3; 2, 70416-69-2; 3, 51293-55-1; 10, 53204-57-2; 14, 4773-82-4; 15, 80540-41-6; 1-methylindene, 767-59-9; 2-methylindene, 2177-47-1; 2-methyl-1-indanone, 17496-14-9; 3-methylindene, 767-60-2; 1,3-dimethylindene, 2177-48-2; 1,1-dimethylindene, 18636-55-0; 1,1,3-trimethylindene, 2177-45-9; 1,2-dimethylindene, 70063-93-3; 2-indanone, 83-33-0; 2-ethyl-3-methylindene, 66703-20-6; 1-ethyl-3-methylindene, 52750-21-7; 3-ethyl-1-methylindene, 26084-58-2; 3-methyl-1-indanone, 6072-57-7; (+)-1-methyl-2-(trideuteriomethyl)indene, 80540-42-7; cyclopentadiene, 542-92-7; 8,9-benzo-10,10-dimethyltricyclo[5.2.1.0<sup>2,6</sup>]dec-8-ene, 80540-43-8; cyclopentene, 142-29-0; 2-methylindene dimer, 80559-48-4; indene, 95-13-6; 2-ethylindene, 17059-50-6.

## Acid-Catalyzed Photoisomerization of 2-Alkylindenes to 2-Alkylindeneindanes<sup>1,2</sup>

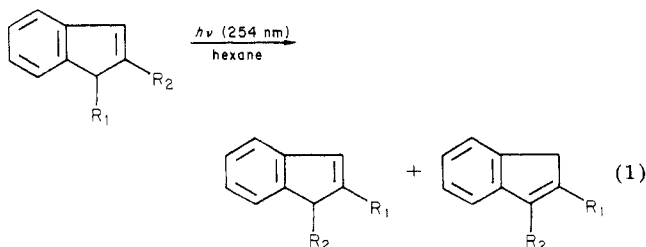
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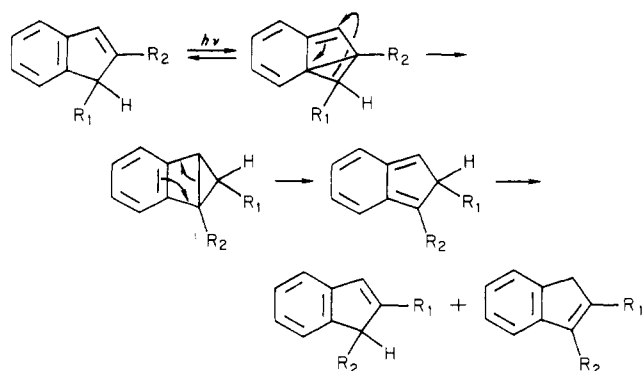
Photolysis of 2-alkylindenes in aprotic media containing hydrochloric acid leads to the formation of 2-alkylindeneindanes with concomitant quenching of the previously reported phototransposition reaction. Quantum efficiencies range from 0.02 to 0.1 and, as with the transposition reaction, are highest for those indenes having short singlet lifetimes. Though there is evidence that the reaction is derived from the singlet excited state, acid has no effect on fluorescence and therefore intervenes by protonating an intermediate formed from  $S_1$ . This intermediate (proposed as the bicyclopentene "I") is common to both the transposition and the olefin migration (cf. Scheme III).

We have, in recent years, reported on a photochemical skeletal rearrangement of alkylindenes which has the net effect of interchanging carbons 1 and 2 (eq 1).<sup>1,3,4</sup> A



mechanism has been proposed<sup>1,3,4</sup> which involves closure

Scheme I. Proposed Mechanism for the Alkylindene Phototransposition



of the alkylindene to a bicyclopentene, a [1,3] sigmatropic shift, opening to an isoindene and 1,5 hydrogen shifts to form the new indenes (Scheme I). During the course of these studies, we came upon a second class of indene photorearrangements which involves exocyclic migration

(1) *Organic Photochemistry*, 51. Part 50: Morrison, H., Giacherio, D.; Palensky, F. J. *J. Org. Chem.*, preceding paper in this issue.

(2) Abstracted from the Doctoral Dissertation of D.G., Purdue University, 1980.

(3) Palensky, F. J.; Morrison, H. *J. Am. Chem. Soc.* 1977, 99, 3507. Giacherio, D.; Morrison, H. *Ibid* 1978, 100, 7109.

(4) See also: Padwa, A.; Goldstein, S.; Loza, R.; Pulwer, H. *J. Org. Chem.* 1981, 46, 1858 and preceding papers in this series.

Table I. Products and Quantum Efficiencies for the Acid-Catalyzed Photoisomerization of 2-Alkylindenes<sup>a</sup>

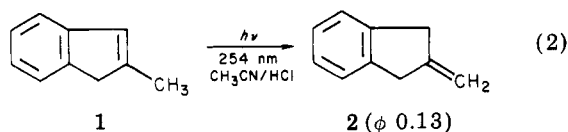
starting indene	product indane	$\phi_{\text{pdt}}$
2-methyl	2-methylene	0.13
1,2-dimethyl	2-methylene-1-methyl <sup>b</sup>	0.10
2,3-dimethyl	2-methylene-1-methyl	0.019
1-ethyl-2-methyl	1-ethyl-2-methylene <sup>c</sup>	0.085
2-ethyl-1-methyl	( <i>E/Z</i> )-2-ethylidene-1-methyl <sup>d</sup>	0.087
3-ethyl-2-methyl	2-methylene-1-ethyl	0.030

<sup>a</sup> Ca. 0.01 M alkylindene in CH<sub>3</sub>CN/0.01 M HCl and using 254-nm light. <sup>b</sup> A small amount of 2,3-dimethylindene is also formed. <sup>c</sup> A small amount of 2-ethyl-3-methylindene is also formed. <sup>d</sup> A small amount of 2-ethyl-3-methylindene is also formed.

of the double bond.<sup>5</sup> It soon became apparent that the two reactions are interrelated, and this paper summarizes our observations on the olefin migration within the context of an overall understanding of alkylindene photochemistry and photophysics.

## Results

**Photolysis of 2-Methylindene (1) in CH<sub>3</sub>CN/Acid or THF/Acid.** This reaction is illustrative of the general observation. A solution of  $8 \times 10^{-3}$  M 1 in acetonitrile containing 0.01 M HCl was photolyzed with 254-nm light to give only one VPC-detectable product (2). Preparative VPC provided a sample, the IR and NMR spectral data for which match well with those in the literature for 2-methyleneindane. The quantum efficiency ( $\phi_2$ ) = 0.13, and photolysis to a 92% loss of 1 gave a 72% yield of 2 (cf. eq 2).

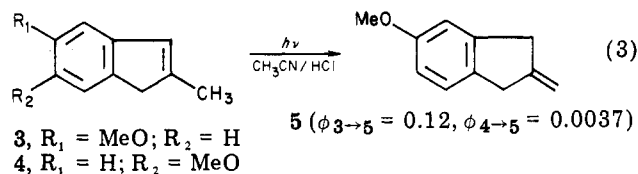


Conversion of 1 to 2 was also observed by using CH<sub>3</sub>CN/0.01 M CF<sub>3</sub>CO<sub>2</sub>H ( $\phi_2$  = 0.019), THF/0.125 M HCl and CH<sub>2</sub>Cl<sub>2</sub> (in which indene sensitization generates HCl in situ). However, neither HClO<sub>4</sub> nor H<sub>2</sub>SO<sub>4</sub> (0.01 M in CH<sub>3</sub>CN) catalyze the formation of 2, though the phototransposition is quenched by these acids as it is for HCl. No VPC-observable products were evident in either the HClO<sub>4</sub> or H<sub>2</sub>SO<sub>4</sub> photolyses though extensive loss of 1 was noted.

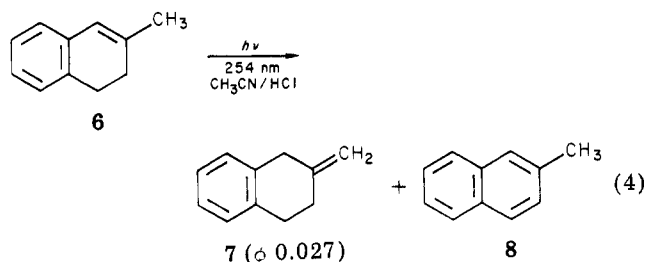
**Alkylideneindane Formation from Other Alkylindenes.** A number of other 2-alkylindenes were photolyzed by using CH<sub>3</sub>CN/0.01 M HCl; our observations are summarized in Table I.

**Photolysis of 5- and 6-Methoxy-2-methylindene in CH<sub>3</sub>CN/HCl.** Irradiation of a ca. 0.01 M solution of a 41.5/58.5 mixture of 5-methoxy- and 6-methoxyindene (3 and 4) results in the formation of a single photoproduct, 5-methoxy-2-methyleneindane (5) with  $\phi_5$  = 0.038<sub>5</sub>. Irradiation of pure 4 gave 5 with  $\phi_{4 \rightarrow 5}$  = 0.0037. Although 3 was unobtainable in pure form, these data and the amount of light absorbed by each isomer in the mixture provide a value of  $\phi_{3 \rightarrow 5}$  = 0.12 (cf. eq 3). Singlet lifetimes of 1.4 and 14.9 ns were measured for 3 and 4, respectively.

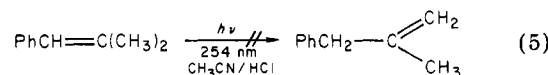
**Photolysis of Related Arylolefins in CH<sub>3</sub>CN/HCl.** Two other substrates were irradiated under the "standard" alkylindene conditions. 3-Methyl-1,2-dihydronaphthalene (6), as a  $7 \times 10^{-3}$  M solution in CH<sub>3</sub>CN containing 0.01 M



HCl, was photolyzed with 254-nm light to give two photoproducts. The major product was 2-methylene-1,2,3,4-tetrahydronaphthalene (7), formed with  $\phi$  = 0.027. The minor product was 2-methylnaphthalene (8; cf. eq 4).

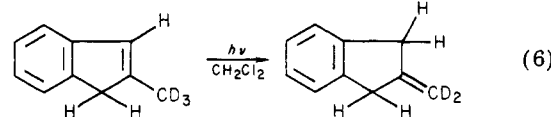


An  $8 \times 10^{-3}$  M solution of 1-phenyl-2-methylpropene (9) in CH<sub>3</sub>CN/0.01 M HCl was irradiated with 254-nm light to 25% loss of 9; no 3-phenyl-2-methylpropene could be detected by VPC (eq 5).

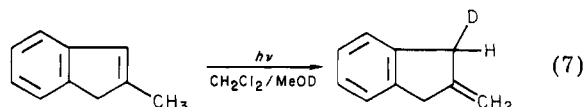


**Triplet Sensitization of 2-Methylindene (1) in CH<sub>3</sub>CN/HCl.** Irradiation of a solution of acetophenone (0.26 M) and 1 (0.015 M) in CH<sub>3</sub>CN/0.01 M HCl with 3100-Å light results in the formation of a dimer of 1<sup>1</sup> but no observable exocyclic olefin 2.

**Photolysis of 2-(Trideuteriomethyl)indene in Dichloromethane.** Photolysis of a 0.01 M dichloromethane solution of the title compound to complete conversion to exocyclic olefin gave a product having a ratio of aromatic/benzylic hydrogens (NMR) of 4.00/3.96 (cf. eq 6).



**Photolysis of 1 in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OD.** A 0.01 M solution of 1 in CH<sub>2</sub>Cl<sub>2</sub> containing 12.5% CH<sub>3</sub>OD was irradiated with 254-nm light. The exocyclic olefin was isolated and analyzed by NMR. Integration indicated a ratio of aromatic/benzylic/vinyl hydrogens of 4.00/3.01/2.00 (cf. eq 7).

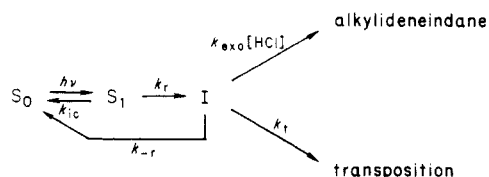


**Effect of HCl on Fluorescence from 1.** The effect of acid on fluorescence was compared to the acid catalysis of olefin photoisomerization and acid quenching of the phototransposition. At a concentration of 0.02 M, HCl decreased the fluorescence of 1 in THF by 2.3%; at this concentration, transposition is quenched by 75%, and exocyclic olefin formation proceeds at 90% of its maximum efficiency (maximum HCl catalysis in THF occurs at 0.125 M).

**Catalysis of Isomerization and Quenching of Transposition as a Function of Acid Concentration.** A series of solutions of 1 in THF containing varying concentrations of HCl were photolyzed at 254 nm and ana-

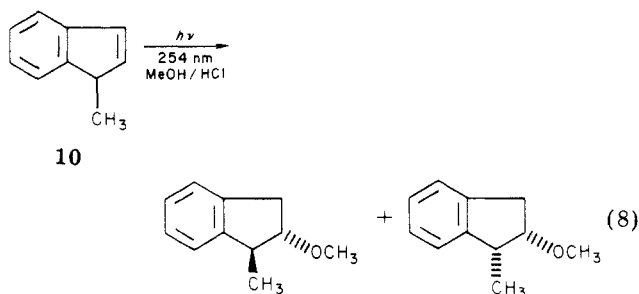
(5) For a preliminary report, see: Morrison, H.; Giachero, D. *J. Chem. Soc., Chem. Commun.* 1980, 1080.

Scheme II. Kinetic Scheme for Alkylindene Rearrangements Involving a Common Intermediate



lyzed for transposition products and exocyclic olefin. The data are presented and discussed in the discussion section.

**Photolysis of 1-Methylindene (10) in Methanol.** Irradiation of an  $8 \times 10^{-3}$  M solution of 10 in 0.25 M methanolic HCl at 254 nm results in the formation of two major products. These were isolated as an 80/20 mixture by VPC and identified as *trans*- and *cis*-2-methoxy-1-methylindane (4:1 *trans*/*cis*; eq 8). Photolysis in 0.25 M



methanolic  $H_2SO_4$  gave results similar to those for HCl. When 1,3-dimethylindene is irradiated in a comparable fashion, there is a gradual loss of starting material but no observable (by VPC) photoproducts. 2-Methylindene gives a mixture of four products: two indenes resulting from transposition, an exocyclic olefin, and a tertiary ether.

### Discussion

**(A) Indene-Indane Photoisomerization.** The results demonstrate that 2-alkylindenes may undergo an acid-catalyzed photoisomerization which leads to 2-alkylideneindanes. The reaction can be synthetically useful and represents the method of choice for preparing 2-methyleneindane<sup>6</sup> (cf. eq 2). Several features of the reaction are noteworthy.

(a) Quantum efficiencies are ca. 0.1 for reactive indenes with HCl, comparable to that observed for the phototransposition of alkylindenes in hydrocarbon solvent.<sup>1</sup>

(b) The nature of the acid catalyst is critical. Trifluoroacetic acid and hydrochloric acid catalyze the reaction, though the latter is considerably more efficient. Perchloric and sulfuric acids are ineffective.

(c) The olefin migration is *not* the result of an intramolecular 1,3 hydrogen shift (cf. eq 6). The hydrogen which is incorporated at C<sub>3</sub> is provided by the medium as a proton (cf. eq 7).

(d) Alkyl substitution at C<sub>3</sub> inhibits the isomerization (cf. Table I) as it does the transposition.<sup>1</sup> The effects of substitution on the aromatic ring are also striking, with marked inhibition by the 6-methoxy group (eq 3).

(e) An (at least superficially) similar reaction is observed in the dihydronaphthalene series (eq 4), but no comparable transformation could be detected for an acyclic (e.g., styrene) derivative (eq 5).

(f) The olefin photoisomerization is seemingly singlet derived (as is the phototransposition),<sup>1</sup> with photoreactivity

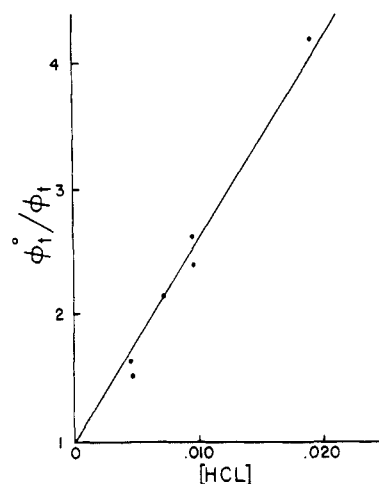


Figure 1. Quenching plot for transposition of 2-methylindene as a function of HCl concentration.

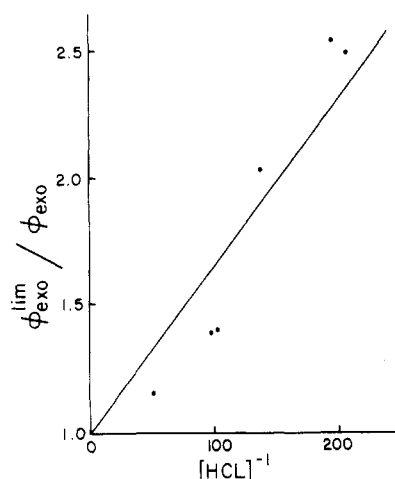


Figure 2. Catalysis plot for exocyclic olefin formation from 2-methylindene as a function of inverse HCl concentration in THF.

inversely correlating with  $1\tau$ . This correlation, noted previously<sup>1</sup> for the transposition, extends to an aryl-substituted indene; the reactive 5-methoxy-2-methylindene has a  $1\tau$  of 1.4 ns, whereas the unreactive 6-methoxy isomer has a  $1\tau$  of 15.0 ns.

(g) Olefin migration occurs at the expense of (i.e., with quenching of) phototransposition. This suggests that the *two reactions have a common intermediate*. However,  $S_1$  (though it is the origin of both reactions) is *not* where bifurcation occurs *since acid has no effect on fluorescence*.

**(B) Kinetic Evidence for the Common Intermediate.** The observations summarized in f and g are nicely rationalized by the sequence outlined in Scheme II, with acid intercepting a common intermediate ("I"), whence one or more steps result in alkylideneindane.<sup>7</sup> This scheme is readily tested.

Let us define the quantum efficiencies for transposition in the absence ( $\phi_t^0$ ) and presence ( $\phi_t$ ) of acid as in eq 9 and 10. Division of the two expressions (Stern-Volmer

$$\phi_t^0 = \frac{k_r}{k_r + k_{ic}} \frac{k_t}{k_t + k_{-r}} \quad (9)$$

$$\phi_t = \frac{k_r}{k_r + k_{ic}} \frac{k_t}{k_t + k_{-r} + k_{exo}[HCl]} \quad (10)$$

treatment) provides eq 11, or with  $\alpha = k_{exo}/(k_t + k_{-r})$ , eq

(6) Palensky, F., Doctoral Dissertation, Purdue University, 1977, and references therein.

(7) For a discussion of the  $k_{ic}$  and  $k_{-r}$  terms, see ref. 1.

12. We may likewise define the quantum efficiency for

$$\phi_t^\circ / \phi_t = 1 + \frac{k_{\text{exo}}[\text{HCl}]}{k_t + k_{-r}} \quad (11)$$

$$\phi_t^\circ / \phi_t = 1 + \alpha[\text{HCl}] \quad (12)$$

formation of alkylideneindane (or its precursor(s)) as  $\phi_{\text{exo}}$  (eq 13), with the "limiting efficiency" ( $\phi_{\text{exo}}^{\text{lim}}$ ) being that

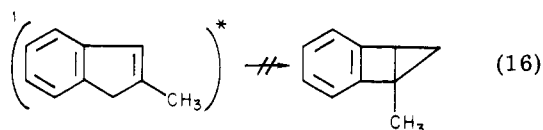
$$\phi_{\text{exo}} = \frac{k_r}{k_r + k_{\text{ic}}} \frac{k_{\text{exo}}[\text{HCl}]}{k_t + k_{-r} + k_{\text{exo}}[\text{HCl}]} \quad (13)$$

$$\phi_{\text{exo}}^{\text{lim}} = k_r / (k_r + k_{\text{ic}}) \quad (14)$$

$$\phi_{\text{exo}}^{\text{lim}} / \phi_{\text{exo}} = 1 + \frac{k_t + k_{-r}}{k_{\text{exo}}[\text{HCl}]} = 1 + \frac{1}{\alpha[\text{HCl}]} \quad (15)$$

which occurs when all of "I" is intercepted by acid (i.e., at  $[\text{HCl}]_{\text{lim}}$ ); cf. eq 14. Stern-Volmer treatment provides eq 15. A comparison of eq 12 and 15 reveals that a (quenching) plot of  $\phi_t^\circ / \phi_t$  vs.  $[\text{HCl}]$  should yield a slope ( $\alpha$ ) which is the reciprocal of the slope of a (catalysis) plot of  $\phi_{\text{exo}}^{\text{lim}} / \phi_{\text{exo}}$  vs.  $[\text{HCl}]^{-1}$ . The data are plotted in Figures 1 and 2;<sup>8</sup> the least-squares-derived values for  $\alpha$  are  $160 \pm 6$  (quenching) and  $145 \pm 14$  (catalysis). Given the nature of these experiments and the separate analysis for indenes and indanes, we believe these data support the proposal embodied in Scheme II.<sup>9</sup>

One important consequence of these conclusions is that we can now put aside a potential mechanism for the phototransposition which we had previously been unable to eliminate, i.e., a concerted "conjugated di- $\pi$ -methane" transformation which converts alkylindene directly into an isomeric bicyclopentene<sup>3</sup> (eq 16). Also eliminated is



a concerted mechanism for double bond migration, such as 1,3 hydrogen shift (see also the isotopic labeling experiments, eq 6 and 7).

(C) **Nature of "I" and Its Conversion to Alkylideneindane.** The indene olefin migration bears a superficial resemblance to the photochemical, acid-catalyzed, endo- to exocyclic olefin migrations in cyclohexenes.<sup>10</sup> However, such reactions proceed via a *trans*-cycloalkene,<sup>10</sup> an intermediate inaccessible to indenes.<sup>11</sup> A reasonable alternative intermediate is the initially formed bicyclopentene already postulated for the phototransposition (cf. Scheme I).<sup>12</sup> The reaction with HCl would then involve

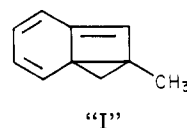
(8)  $\phi_{\text{exo}}^{\text{lim}}$  in THF is reached when  $[\text{HCl}] = 0.125 \text{ M}$ ; the absolute value of  $\phi_{\text{exo}}^{\text{lim}}$  was not determined. It is interesting that  $[\text{HCl}]_{\text{lim}}$  varies appreciably with solvent and appears to correlate with solvent basicity; i.e., by contrast with THF ( $\text{p}K_a(\text{SH}^+) = -3.5$ ), the less basic  $\text{CH}_3\text{CN}$  ( $\text{p}K_a(\text{SH}^+) = -10$ ) has  $[\text{HCl}]_{\text{lim}} = 5 \times 10^{-3} \text{ M}$ , and the very weakly basic  $\text{CH}_2\text{Cl}_2$  is a remarkably reactive medium ( $[\text{HCl}]_{\text{lim}} \leq 10^{-4} \text{ M}$ ). An analogous solvent effect has been noted for the reaction of HBr with unsaturated compounds. Cf.: Reutov, O. A. "Fundamentals of Theoretical Organic Chemistry"; Appleton-Century-Crofts: New York, 1967; pp 210-212.

(9) Note that eq 14 presumes no energy wastage once "I" is protonated by the HCl; in fact, our observations with  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  (wherein quenching, but not catalysis, is observed) suggest that this assumption may not be totally valid.

(10) Dauben, W. G.; van Riel, H. C. H. A.; Robbins, J. D.; Wagner, G. J. *J. Am. Chem. Soc.* 1979, 101, 6383 and references therein.

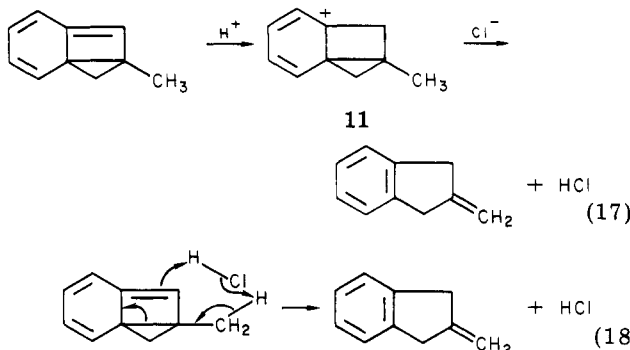
(11) It is possible that the isomerization of dihydronaphthalenes (eq 4) does go through the *trans* olefin, but the direction of the requisite protonation of the *trans* alkene and the lack of 1,4-dihydronaphthalene as a product (a logical precursor to the naphthalene but unobservable in the reaction mixture despite careful analysis by VPC) argue against this mechanism. Further study of this series is in progress.

protonation of "I" at C<sub>3</sub>, in competition with the [1,3]



sigmatropic shift needed for skeletal rearrangement (Scheme I). Evidence that such protonation occurs is provided by experiments in MeOD, wherein deuterium is incorporated at C<sub>3</sub> (eq 7).

The reaction of "I" with acid and the subsequent formation of alkylideneindane may proceed as a stepwise (protonation-deprotonation) sequence (eq 17) or as a concerted reaction (eq 18). An observation which argues



against the concerted mechanism is the ability of  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$  to quench transposition *without* giving alkylideneindane (presumably for lack of a basic counterion).<sup>13</sup> The low quantum efficiency for 6-methoxyindenes (eq 3) may likewise be rationalized as a consequence of destabilization of 11 and a correspondingly reduced  $k_{\text{exo}}$  (cf. Scheme II).<sup>14</sup> Finally, the acid-catalyzed anti-Markovnikov photoaddition of methanol to alkylindenes (cf. eq 8) can be rationalized as an attack by solvent on 11.<sup>17</sup>

If one accepts a protonation-deprotonation sequence (eq 17), one must then explain the contrathermodynamic deprotonation leading to the nonconjugated product.<sup>18</sup> The deprotonation does not appear to involve a second car-

(12) All attempts to directly observe "I" at low temperatures have thus far been unsuccessful. At temperatures ranging from 0 to  $-196^\circ \text{C}$ , neither UV nor NMR analysis gave evidence of this species. When neutral solutions of indenes were irradiated at  $-40$  to  $-78^\circ \text{C}$ , held for 1-2 s in the dark, and then treated with cold HCl solutions, no exocyclic olefin was formed. At such temperatures, photolysis of acidic solutions generates alkylideneindanes.

(13) The mode of action of these acids is uncertain. There is some evidence that less indene is consumed in their presence than with HCl, and no new products are evident. This is suggestive of either (1) an acid-catalyzed pathway for returning "I" to starting indene, which does not involve protonation (i.e., an acid-catalyzed contribution to  $k_{-r}$  in Scheme II), or (2) protonation followed by deprotonation to indene (rather than indane) when a basic counterion is lacking. In one experiment with 2-methyl-1,1,3-trideuterioindene in  $\text{CH}_3\text{CN}/\text{HClO}_4$ , recovered indene gave no evidence of exchange at C<sub>3</sub>, an observation consistent with option 1.

(14) The effect of MeO substitution is clearly manifold and not so simply rationalized. The longer  $^1\tau$  characteristic of the unreactive 6-MeO isomer indicates that closure to "I" ( $k_t$ ) is affected, and there is evidence that the 5-methoxy isomer, though it successfully gives alkylideneindane, resists transposition (cf.  $k_p$ ). We have no explanation for either of these observations; neither frontier orbital arguments<sup>15</sup> nor  $\Delta p$  calculations<sup>16</sup> (both based on extended Hückel calculations) have provided us with any insights. Further theoretical analyses, in collaboration with Dr. Bernard Bigot, are in progress.

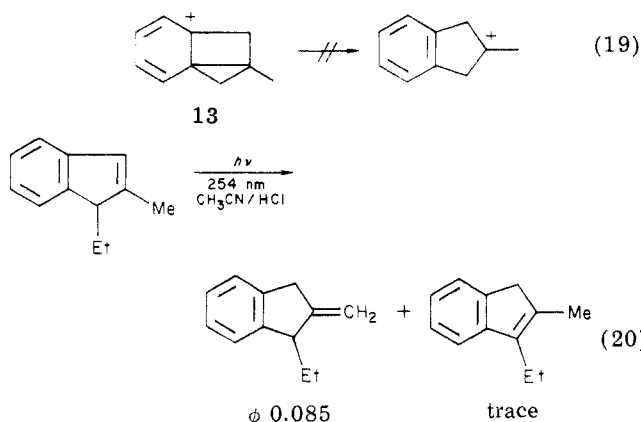
(15) Ku, A. Y.; Paquette, L. A.; Rozeboom, M. D.; Houk, K. N. *J. Am. Chem. Soc.* 1979, 101, 5981 and other papers in this series.

(16) Zimmerman, H. E.; Gruenbaum, W. T.; Klun, R. T.; Steinmetz, M. G.; Welter, T. R. *J. Chem. Soc., Chem. Commun.* 1978, 228. Zimmerman, H. E.; Steinmetz, M. G. *Ibid.* 1978, 230.

(17) Note the ability of sulfuric acid to catalyze the methanol reaction.<sup>13</sup>

(18) It is possible that, with HCl, deprotonation to the original indene also occurs.<sup>5,13</sup>

bonium ion (eq 19) as evidenced by the experiment depicted in eq 20 (cf. Table I).<sup>19</sup> Deprotonation-cyclopropyl



bond cleavage is thus concerted and should be favored by an antiperiplanar relationship between the departing proton and the bond being broken.<sup>20</sup> A model of 11 indicates that only the side-chain protons achieve this optimal relationship (the dihedral angles for the ring hydrogens are 60–70 °C).

**(D) Substituent Effects on the Alkylindene Rearrangements.** We have already noted the curious ability of an alkyl group at C<sub>3</sub> to inhibit both phototransposition ( $\phi_{\text{trans}}$ )<sup>1</sup> and olefin migration ( $\phi_{\text{exo}}$ ), while increasing  $^1\tau$ .<sup>1</sup> Though we cannot explain the effect on  $^1\tau$ ,<sup>14</sup> having data for a second reaction of "I" now allows us to analyze substitution effects on transposition in a manner which was hitherto unavailable. The  $\phi_{\text{trans}}/\phi_{\text{exo}}$  ratios for 2-methylindene and 2,3-dimethylindene are 0.38 and 0.15, respectively. If one assumes the bicyclopentenes ("I") are trapped by HCl and thence converted to exocyclic olefin equally efficiently for the two substrates, the [1,3] sigmatropic shift in 2,3-dimethylindene is 0.15/0.38 (39%) as efficient as that for 2-methylindene. This is presumably caused by a steric inhibition, and a comparison of 1-ethyl-2-methyl- and 1,2-dimethylindene is consistent with such a conclusion. The singlet lifetimes for these substrates are both quite short (1.7 and 1.2 ns, respectively), implying high reactivity. However, the 10-fold lower  $\phi_{\text{trans}}$  for the 1-ethyl derivative (0.02 vs. 0.25)<sup>1</sup> was seemingly contradictory. We now see that the  $\phi_{\text{exo}}$  values are virtually identical (0.09 vs. 0.10), apparent evidence for a large steric barrier to the [1,3] sigmatropic shift.<sup>21</sup>

**(E) Summary.** With the discovery of a second alkylindene photorearrangement, we have been able to develop an overall picture which ties together diverse photophysical and photochemical data for a variety of substrates (cf. Scheme III). As always, there are questions which remain unanswered, and further experimental and theoretical studies in this area are in progress.

### Experimental Section

Complete experimental details for these studies may be found in the doctoral dissertation of D.G.<sup>2</sup> Salient features are abstracted below.

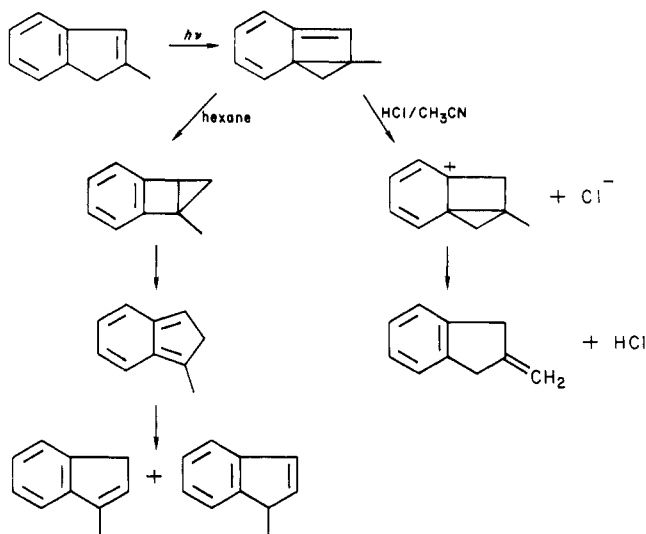
**Instrumentation.** Details of the analytical and photochemical methods have been previously described.<sup>1</sup> VPC columns were as follows: A, 150 ft  $\times$  0.010 in., stainless steel (ss), Golay column

(19) There is also no formation of the 2-methyl-3-ethylindene with sulfuric acid catalysis, indicating that the cyclopropyl cleavage (eq 19) is equally invalid with that acid. (A referee has suggested that protonation could nevertheless lead to the tertiary cation but that kinetically controlled deprotonation might give the exocyclic olefin and starting material rather than the 2-methyl-3-ethylindene.)

(20) Fukui, F.; Fujimoto, H. *Tetrahedron Lett.* 1965, 4303.

(21) Alkoxy substitution has been discussed in footnote 14.

### Scheme III. Alkylindene Singlet Photochemistry



coated with UCON LB-550X; B, 20 ft  $\times$  0.125 in, ss, 20% XF-1150 on 60/80 AW-DMCS Chromosorb W; C, 10 ft  $\times$  0.125 in., ss, 5% SF-96 on 60/80 AW-DMCS Chromosorb W; D, 5 ft  $\times$  0.25 in., aluminum, 10% XF-1150, 10% Bentone on AW-DMCS Gas Pack; E, 10 ft  $\times$  0.375 in., aluminum, 20% Carbowax 20M on 60/80 AW-DMCS Chromosorb W; F, 10 ft  $\times$  0.25 in., aluminum, 10% SE-30 on 60/80 AW-DMCS Chromosorb W; G, 14 ft  $\times$  0.25 in., aluminum, 10% XF-1150 on AW-DMCS 40/60 Gas Pack.

**Syntheses. 2-(Trideuteriomethyl)indene.** Magnesium shavings (1.19 g, 0.049 mol) were placed in a flask equipped with a magnetic stirrer, a static N<sub>2</sub> inlet, a dropping funnel, and a condenser. To the shavings was added 5 mL of a solution of CD<sub>3</sub>I (5.0 g, 0.035 mol) in 25 mL of dry ether. Reaction began immediately, and the remainder of the CD<sub>3</sub>I solution was added dropwise over a 40-min period. The mixture was heated to reflux for 30 min, and most of the ether was then driven off with a stream of nitrogen. To the remaining solution (10 mL) was added, dropwise over a 40-min period, a solution of 2-indanone (3.25 g, 0.0246 mol) in 25 mL of dry benzene. The flask was cooled in an ice bath during the addition. Afterward, the mixture was refluxed for 5 h, cooled, and extracted with 35 mL of hexane. The aqueous layer was again extracted with 35 mL of hexane, and the combined organic layers were dried over MgSO<sub>4</sub> and evaporated to yield 3.30 g (0.0219 mol, 89%) of a yellow oil which later hardened to a waxy solid. Analysis by VPC on column C at 100 °C indicated the complete absence of 2-indanone and the presence of only one volatile component. The crude carbinol (1.78 g, 0.0118 mol) was dehydrated by dissolution in 150 mL of dry benzene containing 50 mg of *p*-toluenesulfonic acid and refluxing for 60 min in a round-bottomed flask fitted with a Soxhlet extractor containing 5-Å molecular sieves. The reaction mixture was cooled, washed with a saturated sodium bicarbonate solution, dried, and evaporated under vacuum. The residual oil was purified by passage in hexane through a 7 cm  $\times$  2.5 cm plug of alumina. This provided 1.24 g (0.0093 mol, 79% crude) of a clear liquid, a portion of which was distilled in a microdistillation apparatus: 83% yield; bp 53–70 °C (bath temperature; 0.1 mm). A portion of the undistilled residue from a separate run on a smaller scale was purified by VPC on column E at 150 °C: IR (neat) 3.22, 3.42, 6.18, 6.83, 7.18, 11.28, 13.02, 13.46, 14.00  $\mu\text{m}$  (small peaks in the 4.4–4.9- $\mu\text{m}$  region, indicative of C–D stretching, were noted); NMR (CDCl<sub>3</sub>)  $\delta$  7.44–7.00 (m, 4 H, aromatic), 6.51 (slightly broadened s, 1 H, vinyl), 3.31 (s, 2 H, benzylic); mass spectrum, calcd for C<sub>10</sub>H<sub>7</sub>D<sub>3</sub> *m/e* 133.097, found *m/e* 133.100.

**6-Methoxy-2-methylindene.** This compound was synthesized in 76% overall yield from 4'-methoxypropiofenone via the Mannich product with dimethylamine hydrochloride and formaldehyde to form the 2-methyl-1-indanone.<sup>22</sup> The crude indanone was reduced with sodium borohydride and dehydrated as described above; purification by VPC on column E at 190 °C pro-

(22) Burkhalter, J. H.; Fuson, R. *J. Am. Chem. Soc.* 1948, 70, 4184.

vided pure indene: IR (neat) 3.48, 6.22, 6.33, 6.79, 6.96, 7.91, 8.09, 8.31, 8.77, 9.00, 9.11, 9.66, 11.65  $\mu\text{m}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  7.21–6.74 (m, 3 H, aromatic), 6.44 (broadened s, 1 H, vinyl), 3.82 (s, 3 H, methoxy), 3.28 (broadened s, 2 H, methylene), 2.12 (broadened s, 3 H, methyl); mass spectrum, calcd for  $\text{C}_{11}\text{H}_{12}\text{O}_2$   $m/e$  160.089, found  $m/e$  160.087.

**5-Methoxy-2-methylindene.** A solution of 1.5 g of crude 6-methoxy-2-methylindene in 5 mL of pyridine was refluxed under nitrogen for 60 min. It was then cooled, poured into 100 mL of 20% HCl solution, and extracted with 50 mL of hexane. The hexane solution was dried over  $\text{MgSO}_4$  and evaporated to yield 1.4 g of a yellow liquid, VPC analysis of which on column A at 145 °C indicated the presence of two components in a ratio of 59/41. Since the major component coeluted with starting material, the minor component was identified as the desired isomer, 5-methoxy-2-methylindene. Preparative separation of the two isomers proved to be extraordinarily difficult. Very small amounts of the pure 5-methoxy compound were isolated by preparative VPC on column D at 170 °C and used for UV absorption and fluorescence emission studies. The unresolved mixture was purified by VPC on column E at 190 °C. Photochemical studies, as well as IR and NMR spectral studies, were performed on the mixture of isomers. The structural assignment of the minor isomer is strengthened by the fact that the IR and NMR spectral data for the mixture are virtually identical with those for the pure 6-methoxy isomer. The spectral data for the 59/41 mixture of 6-methoxy- and 5-methoxy-2-methylindene are as follows: IR (neat) 3.40, 6.21, 6.33, 6.80, 6.99, 7.79, 7.93, 8.10, 8.35, 8.71, 8.80, 9.01, 9.12, 9.66, 11.65  $\mu\text{m}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  7.28–6.09 (m, 3 H, aromatic), 6.43 (broadened s, 1 H, vinyl), 3.76 (s, 3 H, methoxy), 3.22 (broadened s, 2 H, methylene), 2.12 (broadened s, 3 H, methyl).

**trans-1-Methyl-2-indanol.** 3-Methylindene was converted to the indanol by hydroboration–oxidation. Short-path distillation (100–115 °C bath temperature; 1.0 mm) provided a sample for spectral analysis: IR (neat) 2.92, 3.32, 6.73, 6.83, 9.20, 9.35, 9.64, 9.80, 12.89, 13.47, 13.96  $\mu\text{m}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  7.15 (br s, 4 H, aromatic), 4.20–3.99 (m, 1 H, OCH), 3.31–2.65 (m, 3 H, benzylic), 2.21 (s, 1 H, OH), 1.28 (d,  $J = 7$  Hz, 3 H, methyl).

**trans-1-Methyl-2-methoxyindene.** The indanol was etherified by using sodium hydride and methyl iodide. Purification on column F at 145 °C provided an analytical sample: IR (neat) 3.35, 6.77, 6.86, 7.38, 9.00, 10.15, 13.42  $\mu\text{m}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  7.25 (s, 4 H, aromatic), 3.98–3.68 (m, 1, OCH), 3.46 (s, 3 H,  $\text{OCH}_3$ ), 3.35–2.92 (m, 3 H, benzylic), 1.40 (d,  $J = 7$  Hz, 3 H, methyl); mass spectrum, calcd for  $\text{C}_{11}\text{H}_{14}\text{O}$   $m/e$  162.105, found  $m/e$  162.105.

**General Procedure for Exocyclic Olefin Preparation.** The solvent for these preparative photolyses was either spectrograde dichloromethane or a dilute (approximately 0.025 M) solution of HCl in acetonitrile (prepared by diluting concentrated, aqueous HCl with acetonitrile). A solution of approximately 2 mg of endocyclic starting material/mL of solvent (i.e., approximately 0.01–0.015 M) was prepared, added to a low-pressure photolysis well, and irradiated with the Hanovia low-pressure (254 nm) lamp. Dichloromethane solutions were bubbled with argon before and during photolysis; acetonitrile/HCl solutions were not argon bubbled. All reactions could be readily monitored by periodically withdrawing samples for VPC analysis on column A at 134–140 °C. Commonly, a reaction time of 30–50 min was sufficient for 250 mg of starting material (i.e., virtually complete starting material disappearance). After photolysis, dichloromethane solutions were washed with one volume of saturated sodium bicarbonate solution, passed through a short (3 cm  $\times$  10 cm) plug of alumina, and concentrated under vacuum. Acetonitrile solu-

tions were diluted with three volumes of water and extracted with one volume of pentane. The pentane solution was dried and concentrated under vacuum. The exocyclic olefin products were isolated from the concentrated solutions by preparative VPC on column E at 150–180 °C.

**2-Methylene-1-methylindane:** IR (neat) 3.26, 3.31, 3.40, 3.44, 6.05, 6.79, 6.90, 11.42, 12.99, 13.66, 14.04  $\mu\text{m}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  7.12 (s, 4 H, aromatic), 5.03 (br s, 2 H, vinyl), 4.0–3.5 (m, 3 H, benzylic  $\text{CH}_2$  and benzylic CH), 1.38 (d, 3 H,  $\text{CH}_3$ ); mass spectrum, calcd for  $\text{C}_{11}\text{H}_{12}$   $m/e$  144.096, found  $m/e$  144.097.

**1-Ethyl-2-methyleneindane:** IR (neat) 3.20, 3.45, 6.01, 6.76, 6.85, 7.02, 7.29, 8.32, 11.29, 13.45, 13.84  $\mu\text{m}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  7.17 (s, 4 H, aromatic), 5.10 (br s, 2 H, vinylidene), 3.65 (m, 3 H, benzylic), 1.95–1.64 (m, 2 H,  $\text{CH}_2\text{CH}_2$ ), 0.84 (t,  $J = 7$  Hz, methyl); mass spectrum, calcd for  $\text{C}_{12}\text{H}_{14}$   $m/e$  158.110, found  $m/e$  158.109.

**5-Methoxy-2-methyleneindane.** This was prepared by photolysis of the mixture of isomers, with purification on column G at 180 °C: IR (neat) 3.50, 6.20, 6.70, 7.00, 7.58, 7.78, 7.87, 8.02, 8.39, 8.71, 9.01, 9.64, 11.27, 12.25, 12.45  $\mu\text{m}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  7.19–6.72 (m, 3 H, aromatic), 5.15–5.04 (m, 2 H, vinylidene), 3.80 (s, 3 H,  $\text{OCH}_3$ ), 3.68 (br s, 4 H, benzylic); mass spectrum, calcd for  $\text{C}_{11}\text{H}_{12}\text{O}$   $m/e$  160.089, found  $m/e$  160.087.

**2-Methylene-1,2,3,4-tetrahydronaphthalene:** IR (neat) 3.39, 6.03, 6.70, 6.90, 11.28, 13.41  $\mu\text{m}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  7.12 (br s, 4 H, aromatic), 4.89 (br s, 2 H, vinylidene), 3.57 (br s, 2 H,  $\text{ArCH}_2\text{C}=\text{CH}_2$ ), 2.96–2.82 (deformed t, 2 H,  $\text{ArCH}_2\text{CH}_2$ ), 2.56–2.42 (deformed t, 2 H,  $\text{ArCH}_2\text{CH}_2$ ); mass spectrum, calcd for  $\text{C}_{11}\text{H}_{12}$   $m/e$  144.096, found  $m/e$  144.097.

**Photolysis of 1-Methylindene in Methanol.** A solution of 160 mg of 1-methylindene in 200 mL of 0.25 M methanolic HCl (0.006 M in indene) was added to four 50-mL-capacity Vycor tubes. The tubes were photolyzed for 60 min in the Rayonet apparatus with 15 254-nm lamps, at which time VPC analysis on column A at 130 °C indicated substantial starting material disappearance and the appearance of two major products in an 80/20 ratio. The combined solutions were added to 500 mL of water and extracted with 150 mL of hexane. The hexane was removed under vacuum and the product mixture analyzed by NMR and IR. The IR spectrum was identified with that for *trans*-1-methyl-2-methoxyindane (see above), and the NMR spectrum was primarily that of this isomer as well. The minor product was assigned as the *cis* isomer on the basis of a small multiplet ( $\text{C}-\text{H}_3\text{OCH}$ ) at  $\delta$  4.1, 0.35 ppm downfield from the corresponding signal for the *trans* isomer.<sup>23</sup> (There is also a small singlet ( $\text{CH}_3\text{O}$ ) at  $\delta$  3.44, 0.02 ppm upfield from the *trans* isomer.)

**Acknowledgment.** Financial support from the Purdue Research Foundation is gratefully acknowledged.

**Registry No.** 1, 2177-47-1; 2, 68846-65-1; 3, 22138-75-6; 4, 71644-70-7; 5, 71644-78-5; 6, 2717-44-4; 7, 66448-77-9; 8, 91-57-6; 9, 768-49-0; 10, 767-59-9; 1,2-dimethylindene, 70063-93-3; 2,3-dimethylindene, 4773-82-4; 1-ethyl-2methylindene, 70416-69-2; 2-ethyl-1-methylindene, 63265-70-3; 3-ethyl-2-methylindene, 51293-55-1; (*E,Z*)-2-ethylidene-1-methylindane, 80532-50-9; 2-(trideuteromethyl)indene, 80532-51-0; *trans*-1-methyl-2-indanol, 80532-52-1; 3-methylindene, 767-60-2; *trans*-1-methyl-2-methoxyindane, 80532-53-2; 2-methylene-1-methylindane, 76885-44-4; 1-ethyl-2-methyleneindane, 76885-45-5; *cis*-1-methyl-2-methoxyindane, 80532-54-3; 2-(dideuteromethylene)indane, 80532-55-4; 3-deutero-2-methyleneindane, 80532-56-5.

(23) Compare *trans*- and *cis*-2-methylcyclohexanol. "Sadler Research Laboratories NMR Spectra"; Sadler Research Laboratories: Philadelphia, PA, 1966; Spectrum 17117.