

following isotopic composition of the product was obtained: 12% dideuterated, 88% trideuterated.

(IV) 3,7a-Dimethyl-4-hydrindanonones (R = H). (a) Epimers 4a  $\rightleftharpoons$  4b. Isomerization of 4a under the conditions used for 3a required 2 weeks to reach equilibrium. We therefore used the following procedure. To solution of 420 mg of 4a in 6 mL of EtOH was added 2.5 mL of aqueous 2 N KOH. After 3 h of reflux, the extracted product was analyzed by VPC, indicating 69% 4b and 31% 4a.

(b) Epimers 6a  $\rightleftharpoons$  6b. Under the same conditions as for 4a, 6a did not give any detectable 6b. However, enolization at the C3a position was shown by a deuteration experiment as for 5a. The isotopic composition of the product was 2% underated and

13% mono-, 46% di-, and 39% trideuterated. During the deuteration, the  $^1\text{H}$  NMR spectra with  $\text{Eu}(\text{fod})_3$  show that H5 and H5' protons disappear before the H3a proton.

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**Registry No.** 1a, 3513-11-9; 1b, 20480-53-9; 2a, 75961-73-8; 2b, 75961-74-9; 3a, 22647-02-5; 3b, 22646-98-6; 4a, 75961-75-0; 4b, 75961-76-1; 5a, 14800-19-2; 6a, 75961-77-2; cyclohex-2-en-1-one, 930-68-7; 3-methylcyclohex-2-en-1-one, 1193-18-6; acrolein, 107-02-8; methyl vinyl ketone, 78-94-4.

## Sigmatropic Rearrangements of 1,1-Diaryllindenenes.<sup>1-3</sup> Migratory Aptitudes of Aryl Migration in the Ground and Electronically Excited States

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The photochemical and thermal rearrangements of 1,1-diaryllindenenes to give 2,3-diaryllindenenes have been investigated. Migratory aptitudes of *p*-X-phenyl vs. phenyl were determined for X = Br, CN, and OCH<sub>3</sub> in the photochemical and thermal migrations. The identities of the products of these rearrangements were established by unambiguous synthesis, and the synthetic work is described. Product ratios were generally determined by NMR techniques, but VPC and isotope dilution were also used in the case of 1-(*p*-cyanophenyl)-1-phenylindene reactions. The excited-state reactions (direct and triplet sensitized) are highly selective, migration of the substituted phenyl group being favored for all three substituents. The thermal reactions, in contrast, are quite unselective, phenyl migrating almost as readily as the substituted phenyl group in all cases. Quantum yields for the rearrangement in the case of 1,1-diphenylindene and 1-(*p*-cyanophenyl)-1-phenylindene were 0.80 and 0.46, respectively (direct irradiation), and 0.43 and 0.53 (sensitized reactions). The results of the thermal reactions and results from the literature are discussed in terms of bond-dissociation energies and transition-state-delocalization energies calculated by using the Hückel theory. Neither approach led to a satisfactory interpretation. The excited-state migrations are consistent with charge-transfer stabilization of the transition state, which can be estimated from oxidation and reduction potentials by using Weller's equation.

For a number of years we have been studying various aspects of the thermal rearrangements and photorearrangements of 1,1-diaryllindenenes.<sup>1,2</sup> These reactions are of interest for several reasons. First of all, since the migration of phenyl occurs in the ground and excited states<sup>3-5</sup> (i.e., on thermolysis<sup>6,7</sup> and photolysis<sup>1,2,8,9</sup>), studies with suitably substituted indenenes allow a comparison of mi-

gratory aptitudes in the two electronically different states.<sup>1b</sup> Also, photorearrangement of 1,1-diphenylindene (1a) has been proposed to proceed via an isoindene intermediate<sup>1</sup> (2a; see Scheme I). The photoreaction thus promised to be a way of generating various isoindenenes for further study.

We have pursued both lines of research, and in the present paper we describe the synthesis and reactions of various 1,1-diaryllindenenes (1a-d). In a related paper,<sup>2</sup> studies of the isoindene species are described, the latter being observed as transient intermediates. Migratory aptitudes have proved useful in characterizing excited-state properties,<sup>3-5</sup> and the present work provides a comparison between migrations in the ground and excited states.

### Migratory Aptitude Studies

**Syntheses.** (a) Preparation of 1-(*p*-X-Phenyl)-1-phenylindenenes (1). The 1,1-diaryllindenenes 1 were prepared by the route shown in Scheme II. The bromo compound 1b was prepared from 1-(*p*-bromophenyl)-1,1-diphenylpropionic acid (5) by a route similar to the synthesis of 1,1-diphenylindene.<sup>10</sup>

(1) For earlier work in these laboratories, see: (a) J. J. McCullough, *Can. J. Chem.*, **46**, 43 (1968); (b) J. J. McCullough and M. R. McClory, *J. Am. Chem. Soc.*, **96**, 1962 (1974). See also ref 2.

(2) (a) J. J. McCullough and A. J. Yarwood, *J. Chem. Soc., Chem. Commun.*, 485 (1975); (b) K. DeFonseka, C. Manning, J. J. McCullough, and A. J. Yarwood, *J. Am. Chem. Soc.*, **99**, 8257 (1977).

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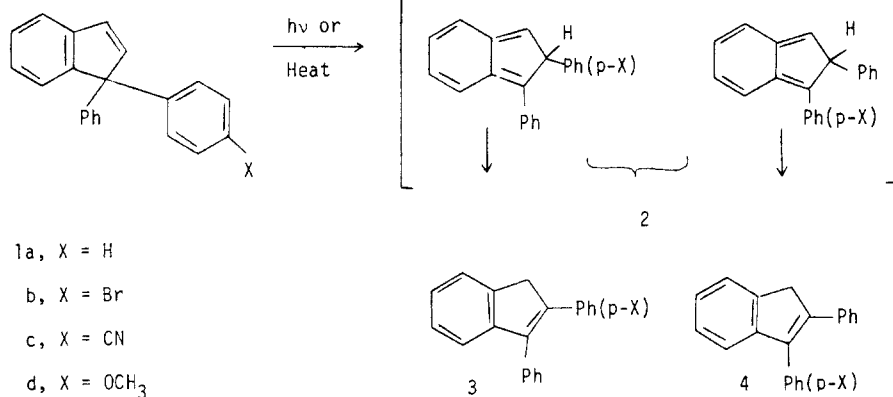
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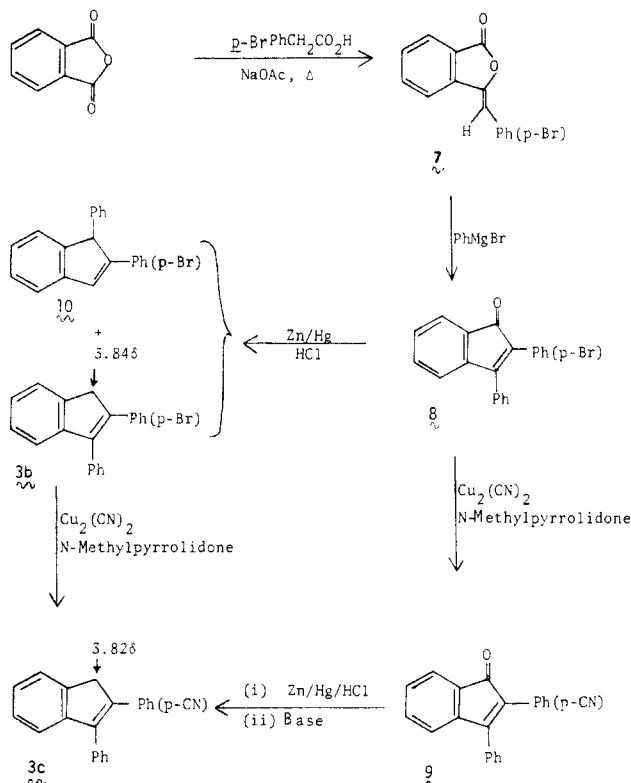
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(10) R. F. Brown and L. M. Jackman, *J. Chem. Soc.*, 3147 (1960).

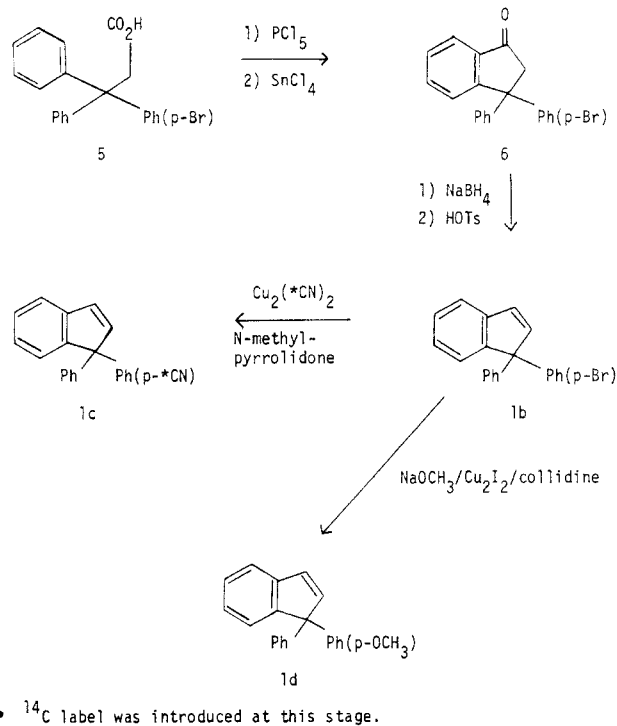
## Scheme I



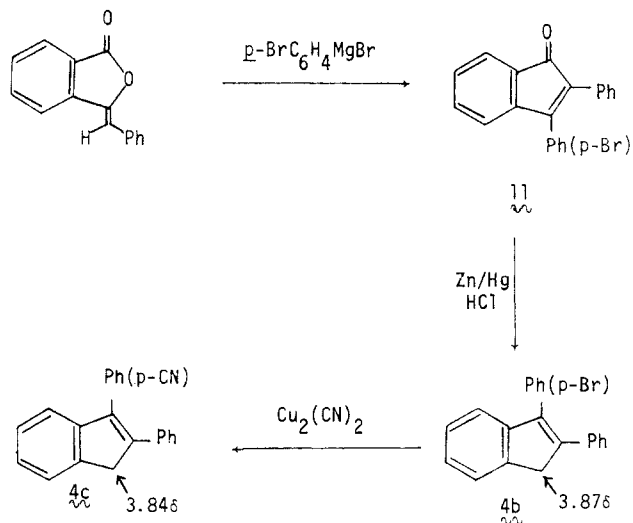
## Scheme II



## Scheme III



## Scheme IV



The *p*-bromo compound was converted into the corresponding cyano and methoxy compounds (1c and 1d, respectively) by use of copper-catalyzed displacements.<sup>11</sup>

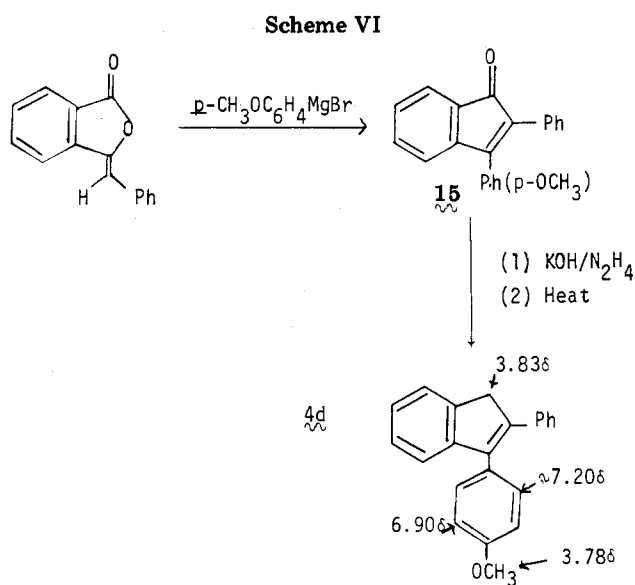
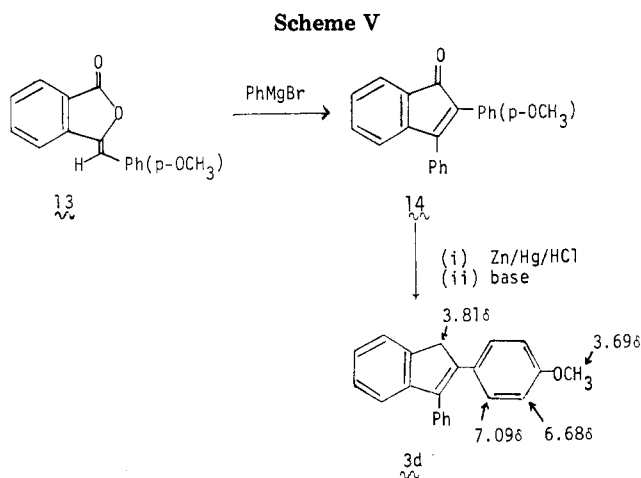
(b) **Preparation of Rearrangement Products.** In principle, four rearrangement products can be derived from each 1-(*p*-X-phenyl)-1-phenylindene on successive 1,5 phenyl and hydrogen shifts. These are, of course, 3, 4, and the corresponding  $\Delta^{1,2}$  isomers,<sup>1a</sup> however, in practice only the  $\Delta^{2,3}$  products are obtained. Under thermolysis conditions, the 1,5 hydrogen shift is rapid,<sup>7</sup> and at 250 °C the  $\Delta^{1,2}$  isomers are converted into the more stable  $\Delta^{2,3}$  compounds, 3 and 4.<sup>12</sup> In the photoreactions, all four products are formed initially (cf. ref 1a), but the  $\Delta^{1,2}$  isomers were isomerized cleanly and quantitatively to the  $\Delta^{2,3}$  compounds by treatment with diethylamine in pyridine.<sup>13</sup> Thus, the analytical problem was a matter of determining

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the ratios of 3 to 4, and only these  $\Delta^{2,3}$  isomers needed to be synthesized.



The synthetic routes to **3** and **4** were similar to that of Shriner and Knox<sup>12</sup> and utilized the appropriate benzylidene phthalides as intermediates. The syntheses are outlined in Schemes III–VI. The *p*-bromo and *p*-cyano compounds (**3b** and **3c**, respectively) were prepared as shown in Scheme III. The (*p*-bromobenzylidene)phthalide **7** was converted to the indenone **8** by treatment with phenylmagnesium bromide. Indenone **8** was transformed into **3b** or **3c** by suitable reduction and displacement with cuprous cyanide.<sup>11</sup>

The products of phenyl migration **4b** and **4c** were prepared according to Scheme IV. Benzylidenephthalide gave 3-(*p*-bromophenyl)-2-phenylidenone (**11**) on reaction with the semi-Grignard reagent from *p*-dibromobenzene. The bromoindenone was reduced to afford 3-(*p*-bromophenyl)-2-phenylindene (**4b**), which was converted to 3-(*p*-cyanophenyl)-2-phenylindene (**4c**).

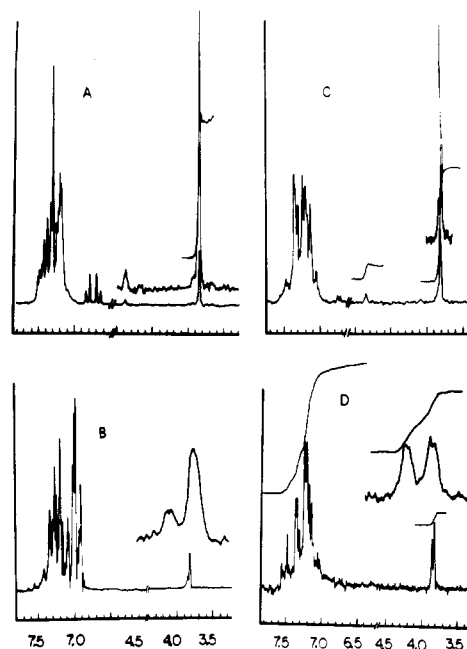
To synthesize the *p*-methoxyphenyl derivatives, **3d** and **4d**, we employed the routes shown in Scheme V and VI, respectively. Since the displacement of aryl bromide with methoxide proceeds in rather poor yield, these compounds were prepared from reagents which already contained the methoxy group. Both routes employed the appropriate benzylidenephthalides, which were converted to **3d** and **4d** as described above for the corresponding bromo compounds.

**(c) Reactions and Analysis of Products.** In the photochemical reactions, the diarylidene **1** (50–200 mg) in 300–400 mL of hexane or *tert*-butyl alcohol was irra-

**Table I. Migratory Aptitudes in Rearrangements of 1-(*p*-X-phenyl)-1-phenylindenes**

	X	solvent	% reaction	ratio of 3/4 <sup>a</sup>
ultraviolet irradiation	CN	hexane	59	>98:2
	CN	ethanol	75	>99.7:0.3 <sup>b</sup>
	CN	decalin		>98:2 <sup>c</sup>
	Br	hexane	88	86:14
	Br	decalin		86:14 <sup>c</sup>
	OCH <sub>3</sub>	hexane	89	95:5
acetophenone sensitization	CN	ethanol	62	>99.7:0.3 <sup>b</sup>
	Br	hexane	78	72:28
thermolysis at 258 °C	CN	diphenyl ether	100	82:18
	Br	diphenyl ether	100	52:48
	OCH <sub>3</sub>	diphenyl ether	100	50:50

<sup>a</sup> All ratios were determined by NMR assay, except where otherwise stated. <sup>b</sup> Ratio was determined by isotope dilution; see Table II. <sup>c</sup> Irradiations were at 130 °C; all others were at 25 °C.



**Figure 1.** 100-MHz NMR spectra of crude reaction mixtures: A, photolysis of 1-(*p*-cyanophenyl)-1-phenylindene; B, thermolysis of 1-(*p*-cyanophenyl)-1-phenylindene; C, photolysis of 1-(*p*-bromophenyl)-1-phenylindene; D, thermolysis of 1-(*p*-bromophenyl)-1-phenylindene.

diated with a 450-W Hanovia lamp. The solution was purged with argon and stirred, and aliquots were removed and analyzed by VPC or NMR. The aliquots were treated with diethylamine in pyridine,<sup>13</sup> as described above, and the ratios of **3** to **4** were measured from the ratios of their methylene group resonances (singlets) in the NMR. In the case of 1-(*p*-methoxyphenyl)-1-phenylindene (**1d**) resonances in the aromatic region were used, because the singlets of the methoxy groups overlapped with those of the methylene groups of the products. In all cases, the NMR spectra were calibrated by using mixtures of authentic products, synthesized as described above. The migratory aptitudes obtained are given in Table I, typical spectra from which the ratios were determined are shown in Figure 1, and the key chemical shifts are given in Schemes IV–VI.

The NMR spectrum of the crude mixture obtained upon irradiation of 1-(*p*-cyanophenyl)-1-phenylindene (**1c**) showed that no “phenyl-migrated” rearrangement product was formed. For confirmation of this result, a careful search for this product was made by using isotope dilution.

**Table II. Direct and Sensitized Quantum Yields in Rearrangement of 1-(*p*-Cyanophenyl)-1-phenylindene**

run <sup>a,c</sup>	[1-( <i>p</i> -cyanophenyl)-1-phenylindene], <sup>e</sup> mM	sensitizer (concn, M)	quantum yield, <sup>b,c</sup> mol einstein <sup>-1</sup>
1	1.18	-	0.43
2	1.18	-	0.48
3	4.13	DCB <sup>d</sup> ( $5.03 \times 10^{-2}$ )	0.51
4	4.13	PhCOCH <sub>3</sub> ( $4.42 \times 10^{-2}$ )	0.55
5	1.18	-	<0.001
6	4.13	DCB <sup>d</sup> ( $5.03 \times 10^{-2}$ )	<0.001

<sup>a</sup> A monochromator, an optical bench, and ferrioxalate actinometry were used in all runs. Irradiation was at 275 nm in direct runs and at 370 nm in sensitized runs.

<sup>b</sup> Light corrected for absorption by products in all runs.

<sup>c</sup> Assay was by isotope dilution. In runs 1-4, the major product 3c was assayed; in runs 5 and 6, assay was for the minor product 4c. The solvent was ethanol in runs 1, 2, and 5 and benzene in 3, 4, and 6. <sup>d</sup> 4,4'-Dichlorobenzophenone. <sup>e</sup> All with <sup>14</sup>CN.

<sup>14</sup>C-Labeled reactant [1-(*p*-cyanophenyl)-1-phenylindene] was prepared by the route in Scheme II using Cu<sub>2</sub>(<sup>14</sup>CN)<sub>2</sub>. After irradiation, unlabeled 3-(*p*-cyanophenyl)-2-phenylindene (4c) was added, and this was purified to constant activity and melting point. From the results (see Experimental Section) the amount of phenyl migration in the photolysis of 1c can be put at less than 0.3%.

In this experiment, quantum yields (formation of 3c) for the reaction were determined by using the major product 3c and the "cold" carrier to assay, with the usual actinometry. These results are given in Table II.

The thermal reactions were conducted by heating 50-100 mg of the 1,1-diarylidene in diphenyl ether (2-3 mL) at reflux (258 °C) under nitrogen of 18-24 h. Two products were found in each case (the 2,3-diphenylindene derivatives 3 and 4), and the ratios of these products were determined as described above. These results are also given in Table I, and typical analytical NMR spectra are shown in Figure 1.

**Spectra of the 1,1-Diarylidenes.** To determine if the different substituents affected the excitation energies of this series of indenenes, we determined the absorption and emission spectra of the compounds. The 0-0 band energies (S<sub>0</sub>-S<sub>1</sub>) from room-temperature absorption and 77 K fluorescence spectra as well as the S<sub>0</sub>-T<sub>1</sub> energies from phosphorescence at 77 K are given in Table III. The 0-0 bands from fluorescence at 77 K and those from absorption coincide.<sup>14,15</sup> Also, the energies of the 0-0 bands for the singlets (from absorption and fluorescence) and for the triplets (from phosphorescence) are relatively insensitive to the indene structure. Evidently, a change in substituent from methyl to substituted phenyl has little effect on the energies of the excited states in this series. Apparently, in all of these compounds, the excitation is localized in the styrene chromophore.

## Discussion

**Multiplicity of Photorearrangements.** It was found earlier that the photorearrangement of 1,1-diarylidenes

could be sensitized by using triplet sensitizers such as acetophenone.<sup>1</sup> Quantum yields for the reactions are given in Tables II, IV, and V; only 1,1-diphenylindene and 1-(*p*-cyanophenyl)-1-phenylindene have been studied. For 1,1-diphenylindene, the quantum yields are lower on triplet sensitization than on direct irradiation. The quantum yield for the triplet rearrangement is 0.44. Correction was made for light absorbed by products in the reaction. There should be little inefficiency in energy transfer from acetophenone to the indene, since a calculation using values of  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the diffusion rate constant<sup>16</sup> and  $2.78 \times 10^6 \text{ s}^{-1}$  for the decay rate of the acetophenone triplet<sup>17</sup> gives a transfer efficiency of almost 90% at  $4.3 \times 10^{-3} \text{ M}$  indene, the lowest indene concentration used. Energy transfer should be diffusion controlled ( $E_T \approx 70 \text{ kcal/mol}$  for acetophenone and 60.5 kcal/mol for indenenes; see Table III). Benzophenone gives the same quantum yield, while Michler's ketone gives a lower quantum yield (0.29), indicating that transfer may not be diffusion controlled with the latter. The quantum yield is independent of diphenylindene concentration (Table V), showing that quenching of the triplet by ground-state diphenylindene is not important, in contrast to DeBoer's finding for the parent indene.<sup>18</sup>

On direct irradiation (Table IV) the quantum yields for 1,1-diphenylindene rearrangement are higher than on sensitization. This must mean that the rearrangement upon direct irradiation involves the singlet excited state of the indene. In the case of 1-(*p*-cyanophenyl)-1-phenylindene (Table II), the quantum yields for direct and sensitized reactions are similar. It is likely that different multiplicities are involved in this case also, since intersystem crossing efficiencies of aromatic hydrocarbons are usually much less than unity.<sup>19</sup> Thus, although the migratory aptitudes in Table I are similar for the direct and sensitized reactions, the two probably involve excited singlet and triplet states, respectively.

**Migratory Aptitudes. (a) Thermal Reactions.** Since the early work of Miller<sup>7</sup> and ourselves<sup>1</sup> on sigmatropic reactions in the indene system, the problem of migratory aptitudes in ground-state migrations has received considerable attention. Although some of the factors which are important have been determined, there is still no generally useful model which can be used to predict rates or relative migratory aptitudes. Some results on indenenes, isoindenenes, and cyclopentadienes which must be explained are as follows.

(i) Hydrogen migrates much more readily than alkyl groups, although both reactions are orbital-symmetry allowed. For example, in cyclopentadienes the 1,5 hydrogen shift has  $E_a = 23.0 \text{ kcal/mol}$ ,<sup>20</sup> while the 1,5-methyl shift has  $E_a = 41-46 \text{ kcal/mol}$ .<sup>21</sup> Hydrogen migrates readily on thermolysis of indenenes,<sup>7</sup> (giving isoindenenes), while the corresponding alkyl shift has not been reported. In the reverse, isoindene-indene conversion, hydrogen migration<sup>2b</sup> has  $E_a = 13.1 \text{ kcal/mol}$ , while methyl migration<sup>22</sup> has  $E_a = 26.1 \text{ kcal/mol}$ . Thus, the activation energies for the hydrogen migration are significantly lower than for methyl in these reactions.

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(19) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, 1970, p 251.

(20) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

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(22) W. R. Dolbier, K. E. Anapole, L. McCullagh, K. Matsui, J. M. Riemann, and D. Rolison, *J. Org. Chem.*, **44**, 2845 (1979).

(14) If the fluorescence spectrum is taken in liquid solution, a significant shift in the 0-0 band relative to the absorption spectrum is observed.<sup>15</sup>

(15) C. A. Parker, "Photoluminescence of Solutions", Elsevier, Amsterdam, 1968, p 13.

Table III. Spectroscopic Properties of 1,1-Disubstituted Indenes

indene derivative	absorption, <sup>a</sup> $\lambda_{\max}$ , nm ( $\epsilon_{\max}$ )	fluorescence, <sup>b</sup> $S_1$ of 0-0 band, nm	phosphorescence, $T_1$ of 0-0 band, nm
1,1-dimethyl	258 (9200)	292.6 <sup>c</sup>	463
1,1-diphenyl	260 (6250)	297.7 <sup>c</sup>	472
1-phenyl-1- <i>p</i> -methoxyphenyl	262 (7100)	297	470
1-phenyl-1- <i>p</i> -bromophenyl	262 (7100)	297	465
1-phenyl-1- <i>p</i> -cyanophenyl	255 (10800)	298	470

<sup>a</sup> Hexane solution. <sup>b</sup> Measured in a polycrystalline matrix of methylcyclohexane. 0-0 band energy was taken as the point of intersection of the fluorescence and absorption bands. <sup>c</sup> Measured in a high-resolution spectrometer; other emission spectra were measured on the Aminco spectrofluorimeter.

Table IV. Quantum Yields for Direct Irradiation of 1,1-Diphenylindene

run	$10^4$ [1,1-diphenylindene], M	quantum yield, <sup>c</sup> mol einstein <sup>-1</sup>
1 <sup>a</sup>	6.49	0.84
2 <sup>a</sup>	6.49	0.80
3 <sup>b</sup>	17.8	0.75

<sup>a</sup> Measured on macroscale bench by using chemical filters. Filters were 5-cm paths of each of the following: (i) 276 g/L of NiSO<sub>4</sub> in water; (ii) 215 g/L of CoSO<sub>4</sub>·7H<sub>2</sub>O in water; (iii) 0.050 g/L of KI and 0.022 g/L of I<sub>2</sub> in water. Filter iv was a 1-cm path of chlorine gas at 1 atm. This combination had 3% transmittance at 258 nm and 0% at 245 and 270 nm. The solvent for reaction was ethanol. <sup>b</sup> Measured by using the monochromator apparatus, in spectrograde hexane as solvent. The wavelength of irradiation was 275 nm. <sup>c</sup> Corrected for light absorbed by products. <sup>d</sup> Assay was by VPC.

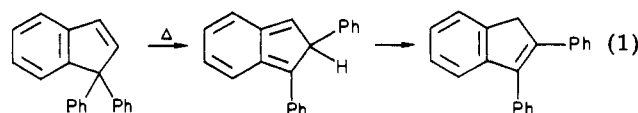
Table V. Quantum Yields for Sensitized Rearrangement of 1,1-Diphenylindene

run	$10^3$ [1,1-diphenylindene], <sup>a</sup> M	sensitizer (concn, M × 10 <sup>2</sup> )	quantum yield ( $\Phi$ ), mol einstein <sup>-1</sup>
1	4.30	acetophenone (4.07)	0.43
2	5.40	acetophenone (4.07)	0.43
3	10.80	acetophenone (4.07)	0.45
4	19.30	acetophenone (4.07)	0.42
5	19.30	acetophenone (4.07)	0.46
6	5.48	benzophenone (11.2)	0.42
7	5.14	michler's ketone (0.1)	0.29

<sup>a</sup> Benzene solvent. <sup>b</sup> Wavelength of irradiation was 370 nm.

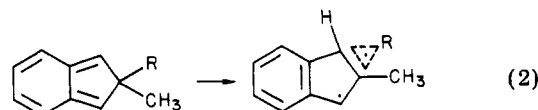
(ii) Unsaturated groups (e.g., vinyl, phenyl, acyl) in indenenes or cyclopentadienes migrate better than alkyl groups, with acyl groups migrating particularly readily.<sup>23-27</sup> Miller and Boyer<sup>7b</sup> found that thermolysis of 1,1-diphenylindene gave 1,2-diphenylindene, via an isoindene

(eq 1). The activation energies reported were 28.3 kcal/mol for 1,1-diphenylindene and 27.7 kcal/mol for 1,1,3-triphenylindene.<sup>7b</sup>



We do not have a model which can satisfactorily account for all the above trends, and, indeed, no such simple model may exist. However, we can point out some factors we believe to be important, on the basis of our results as well as those in the literature.

First we will consider the effect of unsaturation in the migrating group. Miller,<sup>7</sup> Jones,<sup>23-25</sup> and Semmelhack<sup>26,27</sup> have shown that unsaturated groups often migrate better than alkyl groups in indenenes and cyclopentadienes. Perturbation molecular orbital theory has been used in a qualitative way to explain the facile migration of formyl<sup>23,24</sup> and vinyl<sup>26</sup> groups. While interaction of the  $\pi$ -system of the migrating group with that of the indene moiety is undoubtedly important, it is not the only factor. For example, reaction is slow when the migrating group is C $\equiv$ CH or C $\equiv$ N.<sup>23,24</sup> A second factor which in our opinion must be considered is the strength of the  $\sigma$  bond which is partly broken in the transition state for migration. Dolbier<sup>22</sup> has shown that the rate of migration of alkyl groups, in the conversion of 1,1-dialkylisoindenenes into indenenes, parallels the stability of the migrating alkyl radical and thus is related to the bond-dissociation energy of the  $\sigma$  bond being (partly) broken<sup>22</sup> (eq 2). The facile migration of formyl



and acetyl groups<sup>23,24</sup> could be partly due to the stability of the migrating acyl radical. This would also explain the sluggish migration of ethynyl, cyano, and methoxycarbonyl.<sup>23,24</sup> Relevant bond-dissociation energies in kilocalories/mole are as follows:<sup>28,29</sup> CH<sub>3</sub>-H, 104; CH<sub>3</sub>C(O)-H, 87; CH<sub>3</sub>OC(O)-H, 92.7; NC-H, 120; HC $\equiv$ C-H, 125. Thus, thermochemical factors should be borne in mind when these reactions are considered.

We have also used Hückel molecular orbital theory in trying to understand the relationship between structure and reactivity in these 1,5-shifts. This approach was used by Zimmerman and Zweig<sup>30</sup> to interpret 1,2-migrations in

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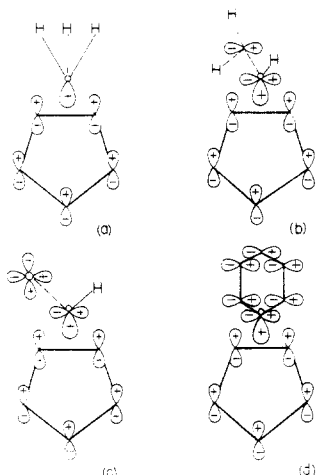
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(29) R. C. West, Ed., "Handbook of Chemistry and Physics", 60th ed., CRC Press, Cleveland, OH, 1979-1980, pp F231-F235.

(30) H. E. Zimmerman and A. Zweig, *J. Am. Chem. Soc.*, **83**, 1196 (1961).



**Figure 2.** Orbital arrays used in Hückel calculations: (a) methyl migration, (b) vinyl migration, (c) formyl migration, (d) phenyl migration.

**Table VI.** Energy Changes on Forming Half-Migrated, Bridged Transition States

reactant (energy, $\beta$ )	transition state <sup>a</sup> (energy, $\beta$ )
methylcyclopentadiene (8.44)	a (8.92)
vinylcyclopentadiene (10.65)	b (10.63)
formylcyclopentadiene <sup>b</sup> (i, 13.48; ii, 17.48)	c (i, 14.75; ii, 17.54)
phenylcyclopentadiene (18.47)	d (17.69)

<sup>a</sup> Letters refer to Figure 2. <sup>b</sup> Entry i neglects the *n* orbital on oxygen; entry ii includes the *n* orbital and assumes *sp* hybridization of carbonyl carbons; i.e., the migrating group resembles the formyl radical.

carbonium ions, radicals, and carbanions. Using Hückel theory, they calculated the energy difference between the reactant (ion or radical) and the transition state for alkyl or phenyl migration and found that the energies obtained agreed very well with the experimental migratory aptitudes.

Our calculations were for migration of various groups (methyl, vinyl, formyl, phenyl) in a thermoneutral reaction in the cyclopentadiene system. Owing to symmetry, a half-migrated transition state is reasonable. Diagrams showing the orbitals used in the transition state models for migration of the four groups of interest are shown in Figure 2. Cyclopropane geometry was assumed for the three carbons of the migration start, terminus, and bridging group. Resonance integrals were taken from the literature<sup>30</sup> where available or were calculated from Mulliken's tables<sup>31</sup> as described by Zimmerman.<sup>30,32</sup> Hückel orbital energies for the reactant molecules (i.e., 5-methyl-, 5-vinyl-, 5-formyl-, and 5-phenylcyclopenta-1,3-dienes) were taken from the literature.<sup>32,33</sup> The calculated energies of activation are given in Table VI. The agreement with experimentally measured activation energies is rather unsatisfactory. The stabilities of the transition states are all exaggerated.<sup>34</sup> For example, the

methyl-bridged configuration (a) is calculated to be 0.48 $\beta$  more stable than the reactant molecule, while the formyl-bridged species is calculated to have the same stability as or greater stability than the corresponding reactant. Phenylcyclopentadiene has a calculated activation energy of 0.78 $\beta$  for phenyl migration, while vinylcyclopentadiene is calculated to have no activation energy for vinyl migration. Experimentally, migration of phenyl has the lower activation energy.<sup>7,23b</sup> Finally, these simple Hückel calculations do not account for the large difference in the activation energies for a 1,5-shift of methyl vs. hydrogen, since the energies of methyl- and hydrogen-bridged species are calculated to be the same. Thus, even to explain qualitative trends in these sigmatropic reactions better calculations will be required.

**Polar Substituent Effects.** These thermal phenyl,<sup>1b</sup> hydrogen,<sup>2b,9</sup> and vinyl shifts<sup>24</sup> are influenced by polar substituents. An electron-withdrawing substituent on the migrating phenyl<sup>1b</sup> or vinyl<sup>24</sup> group favors migration, while similar substituents at the migration start or terminus retard the migration of hydrogen.<sup>2b,9</sup>

Jones<sup>24</sup> proposed a qualitative explanation for the migration of vinyl groups, in which the coefficients of the LUMO of the migrating vinyl group (which depend on the substituent) are important. The faster migration of *p*-cyanophenyl vs. phenyl in 1-(*p*-cyanophenyl)-1-phenylindene might be explained similarly. This perturbation approach should be developed further, and we note that other theoretical approaches have been used in studying 1,5-shifts.<sup>9,35</sup>

**(b) Photochemical Reactions.** The results in Table I show that the substituted phenyl group in 1b-d migrates preferentially on photolysis, and the selectivity is very high—higher than in the ground-state reactions. Note that the data in Table I are relative migratory aptitudes; absolute rates have not yet been measured. The results are consistent with the early work of Zimmerman and co-workers on aryl migrations in enone photochemistry.<sup>3,4</sup> They found that *p*-methoxyphenyl and *p*-cyanophenyl both migrated in preference to phenyl to the  $\beta$ -carbon of an enone system. They proposed that the transition state for migration was radical-like, with considerable odd-electron character on the migrating phenyl group. Our results and those of Hixon<sup>5</sup> are consistent with such a picture. There is, however, an alternate explanation which we advance for consideration. One can regard the diphenylindene system as bichromophoric, one chromophore being the initially excited styrene moiety and the other the migrating aryl group. It is now well-known that interactions in the excited state between chromophores depend on their electron donor-acceptor abilities. The tendency for such interactions to occur between an excited donor (or acceptor) and a ground-state acceptor (or donor), giving a charge-transfer exciplex, is given by Weller's equation<sup>36,37</sup> which for hydrocarbon solvents is given by eq 3.  $\Delta H_f$  is

$$\Delta H_f = -\Delta E'_{0,0} + 23.06[E(D/D^+) - E(A^-/A)] + 3.0 \text{ kcal/mol} \quad (3)$$

the enthalpy of complex formation,  $\Delta E'_{0,0}$  is the singlet

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(32) H. E. Zimmerman, "Quantum Mechanics for Organic Chemists", Academic Press, New York, 1975, pp 131-145.

(33) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961.

(34) The energies in Table VI are in units of  $\beta$ , and a larger value corresponds to a more stable system (more negative energy).

(35) J. R. de Dobbelaere, J. M. F. van Dijk, J. W. de Haan, and H. M. Buck, *J. Am. Chem. Soc.*, **99**, 392 (1977).

(36) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 839 (1969).

(37) A. Weller in "The Exciplex", Academic Press, New York, 1975, p 23.

Table VII. Data<sup>a</sup> Used in Calculation of Heats of Internal Exciplex Formation ( $\Delta H_f$ )

	$E(D/D^+)$ , V	$E(A^-/A)$ , V
1,1-dimethylindene	1.68 <sup>b</sup>	-2.45 <sup>c</sup>
<i>p</i> -methylanisole	1.61 <sup>d</sup>	
<i>p</i> -tolunitrile		-2.45 <sup>e</sup>
toluene	2.20 <sup>f,g</sup>	

<sup>a</sup>  ${}^1\Delta E_{0,0}$  for indene chromophore = 96.2 kcal/mol from above spectra. <sup>b</sup> S. Farid and S. E. Shaler, *J. Chem. Soc., Chem. Commun.*, 677 (1973). <sup>c</sup> C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcell Dekker, New York, 1970. <sup>d</sup> Value for anisole corrected for methyl substitution: A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 4124 (1964). See also footnote c. <sup>e</sup> P. H. Rieger, J. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963). See also footnote c. <sup>f</sup> N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968). <sup>g</sup> All potentials are given vs. the saturated calomel electrode.

excitation energy of the excited partner (0,0 band), and  $E(D/D^+)$  and  $E(A^-/A)$  are the oxidation and reduction potentials, in volts, of the donor and acceptor, respectively.

This equation can be used to calculate  $\Delta H_f$  for internal exciplex formation between the styrene system and a migrating phenyl, *p*-cyanophenyl, or *p*-methoxyphenyl group, respectively. The styrene chromophore was assumed to be the acceptor with phenyl or *p*-methoxyphenyl migrating and the donor with *p*-cyanophenyl migrating. The data used in the calculations are given in Table VII. The values of  $\Delta H_f$  (kilocalories/mole) calculated by using eq 1 are as follows: phenyl migration, 14.0; *p*-cyanophenyl migration, 2.0; *p*-methoxyphenyl migration, 0.42.

$\Delta H_f$  for exciplex formation is thus much more negative when the migrating phenyl group carries a good electron-donating or -withdrawing substituent, and this is in qualitative agreement with the results given in Table I. The same selectivity in the triplet reactions may be due to similar factors. Equation 3 also applies to triplet exciplexes,<sup>37</sup> although  $\Delta E_{0,0}$  is, of course, smaller than for singlets, but the same trend would be followed as in the singlet case.

### Experimental Section

**Materials. General Synthetic Procedures.** Reagents and solvents distilled prior to use were as follows: 1-methyl-2-pyrrolidinone (Eastman, practical), bp 30–32 °C (1 mm); 2,4,6-collidine (Aldrich, analyzed reagent), bp 163–165 °C; *tert*-butyl alcohol (Baker, analyzed reagent), bp 81–82 °C; acetophenone (Fisher, certified reagent), bp 196–198 °C; bromobenzene (Eastern, reagent), bp 153–155 °C; diphenyl ether (Eastern, reagent), bp 54–56 °C (0.5 mm).

Aldrich reagent grade *p*-bromobenzophenone was recrystallized from benzene; mp 81–82 °C. The *p*-bromobenzene (Aldrich, reagent) was recrystallized from ether–petroleum ether; mp 87–89 °C. Other solid reagents used were as follows: (4-bromophenyl)acetic acid (Aldrich, reagent), mp 115–116 °C; (*p*-methoxyphenyl)acetic acid (99%, Aldrich, analyzed reagent), mp 86–88 °C; *p*-bromoanisole (Fisher, highest purity), bp 210–212 °C, mp 13–14 °C.

Ultraviolet spectra were recorded on a Cary 14 spectrophotometer with purified *n*-hexane as solvent. Infrared spectra were obtained on a Perkin-Elmer Model 337 or on a Beckman IR-5 instrument using spectral grade carbon tetrachloride or chloroform as solvent. <sup>1</sup>H NMR spectra were run on a Varian HA-100 instrument using CDCl<sub>3</sub> as solvent and tetramethylsilane as an internal standard. Melting points were taken on a Kofler hot stage and are uncorrected. Fisher alumina absorption was used for column chromatography, while MN-silica gel G/UV<sub>254</sub> (Machery, Nagel, and Co.) was used for thin-layer chromatography (TLC). Elemental analyses were by Dr. A. B. Gygli, Toronto, Ontario, or by Galbraith Laboratories.

**1-(*p*-Bromophenyl)-1,1-diphenylcarbinol.** A solution of 0.30 mol of phenylmagnesium bromide in ether (120 mL) was added under nitrogen to a rapidly stirred solution of 51 g (0.19 mol) of *p*-bromobenzophenone in 300 mL of benzene. A red solution formed instantly, but the color disappeared upon stirring of the mixture overnight, leaving a white flocculent precipitate. The reaction mixture was then added to 200 mL of 3 N H<sub>2</sub>SO<sub>4</sub>, and the aqueous phase was extracted with portions of benzene (3 × 50 mL). Subsequent washing of the combined benzene solutions with 200 mL of 5% NaHCO<sub>3</sub> and then with 200 mL of water followed by drying (MgSO<sub>4</sub>) of the mixture and evaporation of the solvent yielded an orange oil. When the oil was dissolved in ether–hexane and the mixture cooled to 0 °C, there was obtained 40 g of crude brown crystals, mp 92–95 °C. The crude product was chromatographed on a 80 × 4.0 cm column of alumina, slurry packed in hexane, and elution was achieved with 10% ether–hexane. Fractions 10–50 (400-mL fractions) yielded a total of 36 g (0.106 mol, 56%) of 1-(*p*-bromophenyl)-1,1-diphenylcarbinol as colorless needles: mp 99–100 °C; <sup>1</sup>H NMR  $\delta$  2.80 (s, 1 H), 7.30–7.70 (m, 14 H); IR 3400–3500 (s), 3600 cm<sup>-1</sup> (sharp).

**3-(*p*-Bromophenyl)-3,3-diphenylpropionic Acid (5).** A mixture of 3.60 g (0.106 mol) of (*p*-bromophenyl)diphenylcarbinol and 14.3 g (0.138 mol) of malonic acid was heated for 3 h, under nitrogen at 150 °C. Additional portions of 14.3 g of malonic acid were added after the first and second hours of heating. The temperature was raised to 160 °C for 30 min, and the resultant melt was cooled, dissolved in 300 mL of ether, and extracted with portions of 2.5% aqueous potassium hydroxide (2 × 400 mL). The aqueous phase was then acidified with concentrated hydrochloric acid. Cooling to 0 °C produced brown crystals which were filtered and decolorized with carbon in refluxing 95% ethanol. Recrystallization from 95% ethanol gave 26.0 (0.068 mol, 64%) of 5 as colorless needles: mp 190–192 °C; <sup>1</sup>N NMR  $\delta$  3.60 (s, 2 H), 6.90–7.35 (m, 14 H), 10.50 (br s, 1 H); IR 1725 (sharp), 2800–3200 cm<sup>-1</sup> (br).

**3-(*p*-Bromophenyl)-3-phenyl-1-indanone (6).** The ketone 6 was synthesized according to the method of Johnson.<sup>38</sup> A solution of 25.9 g (0.068 mol) of 5 in 50 mL of benzene was stirred and cooled in an ice bath, and 15.6 g (0.075 mol) of phosphorus pentachloride was added during 5 min. Upon removal of the ice bath, the contents of the flask were heated during 20 min (with HCl evolution) to the boiling point, and heating at reflux was continued for 10 min. Then, with continued stirring, the flask was cooled in an ice–salt bath until the internal temperature fell to -10 °C. With continued efficient cooling, there was added over a 15-min period of solution of 38.6 mL (0.34 mol) of stannic chloride in 400 mL of benzene. During this addition, the temperature was maintained below 15 °C. Stirring was continued for 1 h at 0–10 °C after which the solution was allowed to warm to room temperature overnight. The complex was then decomposed by careful addition of 35 g of ice plus 30 mL of concentrated hydrochloric acid. The resultant two-phase mixture was heated under reflux for 2–3 h (a few milliliters of ether were added). The aqueous phase was separated and extracted with portions of benzene (3 × 40 mL). These extracts were combined but kept separate from the original organic phase. Each wash solution was used first with the original organic phase and then with the extracts. The washes used in this sequence were 100 mL of water, 100 mL of 10% Na<sub>2</sub>CO<sub>3</sub>, 100 mL of water, and 50 mL of saturated NaCl solution. The benzene was evaporated after drying (Na<sub>2</sub>SO<sub>4</sub>) to give an oily residue. Addition of ether–petroleum ether gave 18.6 g (0.051 mol, 75%) of crystalline material, mp 87–90 °C. Recrystallization from ether–petroleum ether gave colorless granules of the ketone 6: mp 91–92 °C; IR 1710 cm<sup>-1</sup> (s); <sup>1</sup>H NMR  $\delta$  3.45 (s, 3 H), 6.65–7.50 (m, 13 H). Anal. Calcd for C<sub>21</sub>H<sub>15</sub>BrO: C, 69.43; H, 4.16; Br, 21.99. Found: C, 69.37; H, 4.22; Br, 21.97.

**3-(*p*-Bromophenyl)-3-phenyl-1-indanol.** This indanol was prepared according to the procedure of Brown and Jackman.<sup>39</sup> A solution of 34 g (0.094 mol) of 3-(*p*-bromophenyl)-3-phenyl-1-indanone (6) and 0.88 g (0.024 mol) of sodium borohydride in 500 mL of 95% ethanol was stirred for 48 h at room temperature. A further 3.5 g (0.095 mol) of sodium borohydride was added, and

(38) G. D. Johnson, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, 1963, p 900.

(39) R. F. Brown and L. M. Jackman, *J. Chem. Soc.*, 3144 (1960).

the solution was stirred for an additional 6 h. The solution was then slowly poured into 250 mL of chilled 6 N H<sub>2</sub>SO<sub>4</sub>. The white flocculent precipitate was filtered and washed with water. A methylene chloride solution of the crystals was dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent evaporated to give 28.4 g (0.078 mol, 83%) of the indanol as a white powder with a melting range of 120–170 °C: IR 3300–3500, 3600 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.90 (br s, 1 H), 2.70 (q, *J* = 7.0 Hz, 1 H), 3.25 (q, *J* = 7.0 Hz, 1 H), 5.05 (br t, *J* = 7.0 Hz, 1 H), 6.70–7.40 (m, 13 H). The mass spectrum has a parent peak at *m/e* 365. The product was presumed to be a mixture of stereoisomers which was used in the following dehydration without further purification.

**1-(*p*-Bromophenyl)-1-phenylindene (1b).** The procedure of Brown and Jackman<sup>39</sup> was employed to synthesize the indene 1b. A solution of 25.0 g (0.068 mol) of the indanol from the previous preparation in 400 mL of glacial acetic acid was heated under reflux with 1.8 g (0.01 mol) of *p*-toluenesulfonic acid for 40 min. The mixture was then cooled and poured into 500 mL of water. The solution was extracted with portions of methylene chloride (3 × 150 mL), and the combined extracts were successively washed with portions of 10% Na<sub>2</sub>CO<sub>3</sub> (3 × 100 mL) and 300 mL of water. The organic extracts were dried (Na<sub>2</sub>SO) and concentrated to yield 20.1 g of crude crystalline material, mp 115–117 °C. Recrystallization from ether–petroleum ether gave 19.0 g (0.055 mol, 81%) of 1b as colorless rods: mp 118–119 °C; IR 820, 1010, 1480, 1600, 3065 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 6.67 (AB q, *δ*<sub>A</sub> 6.63, *δ*<sub>B</sub> 6.71, *J*<sub>AB</sub> = 5.0 Hz, 2 H), 6.95–7.40 (m, 13 H). Anal. Calcd for C<sub>21</sub>H<sub>15</sub>Br: C, 72.64; H, 4.35; Br, 23.01. Found: C, 72.93; H, 4.31; Br, 22.86.

**1-(*p*-Cyanophenyl)-1-phenylindene (1c).** The methods of Newman and Boden<sup>11a</sup> and Bacon and Hill<sup>11b</sup> were used. The bromoindene 1b (11.3 g, 0.033 mol) and 5.3 g (0.059 mol) of cuprous cyanide in 30 mL of 1-methyl-2-pyrrolidone were heated at the reflux temperature under nitrogen for 2 h. The reaction mixture was cooled and poured into 8.6 g (0.176 mol) of sodium cyanide in 200 mL of water. The mixture was shaken thoroughly, 500 mL of benzene was added, and the mixture was filtered through Celite. The organic layer was separated and washed with 200 mL of 10% aqueous sodium cyanide solution and then with 300 mL of water. The benzene layer was separated, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to give a black oil. Dissolution of the oil in boiling 95% ethanol with subsequent cooling to room temperature gave 7.9 g of brown granules, mp 147–151 °C.

Recrystallization from 95% ethanol yielded 7.0 g (0.024 mol, 73%) of 1c as colorless granules: mp 152–154 °C; IR 840, 1500, 1600, 2230, 3060 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 6.76 (AB q, *δ*<sub>A</sub> 6.69, *δ*<sub>B</sub> 6.83, *J*<sub>AB</sub> = 5.0 Hz, 2 H), 7.06–7.51 (m, 13 H). Anal. Calcd for C<sub>22</sub>H<sub>15</sub>N: C, 90.07; H, 5.15; N, 4.78. Found: C, 90.08; H, 5.02; N, 4.87.

**1-(*p*-Methoxyphenyl)-1-phenylindene (1d).** The procedure used was that described by Bacon and Rennison.<sup>11c</sup> Freshly cut sodium (0.69 g, 0.03 mol) was added, under nitrogen, to 12 mL of anhydrous methanol in the reaction flask. When dissolution was complete, the warm solution was diluted with 10 mL of dried and redistilled 2,4,6-collidine, followed by 0.95 g (0.005 mol) of vacuum-dried cuprous iodide, the bromoindene 1b (3.47 g, 0.01 mol), and 2,4,6-collidine (30 mL). The mixture was stirred and heated at reflux temperature under nitrogen. After 7 h, an aliquot (2 mL) was taken and added to 10 mL of 6 N HCl and the mixture extracted with fractions of ether (2 × 10 mL) after which the ethereal solutions were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The residue was monitored for the presence of 1d by NMR. After 20 h, the reaction mixture was added to 100 mL of 6 N HCl. Extraction with fractions of ether (2 × 100 mL) and concentration of the ether following drying (Na<sub>2</sub>SO<sub>4</sub>) gave a brown oil that showed three spots (*R*<sub>f</sub> 0.5, 0.6, and 0.7) on TLC (5% ether–petroleum ether). Chromatography of the oil on a 37 × 4 cm column of alumina and elution with hexane gave 200-mL fractions as follows: fractions 6–18 contained 1.0 g of 1,1-diphenylindene, mp 89–90 °C; fractions 20–25 gave 0.20 g of 1-(*p*-bromophenyl)-1-phenylindene (1b). Elution was continued with 2% ether–petroleum ether, and fractions 29–40 gave 0.60 g of crystals, mp 74–76 °C. Recrystallization from petroleum ether gave 0.53 g (0.0018 mol, 19%) of 1d as fluffy needles: mp 77–78 °C; IR 828, 1040, 1188, 1245, 1510, 1605, 2840, 2910, 2960, 3065 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 3.77 (s, 3 H), 6.75–6.84 (m, 4 H), 7.10–7.45 (m, 1 H). Anal. Calcd for C<sub>22</sub>H<sub>18</sub>O: C, 88.56; H, 6.08. Found: C, 88.61; H, 6.02.

***p*-Bromo-3-benzylidene-phthalide (7).** The procedure of Weiss was employed.<sup>40</sup> A mixture of 54.2 g (0.366 mol) of phthalic anhydride, 94.6 g (0.440 mol) of (*p*-bromophenyl)acetic acid, and 1.4 g (0.017 mol) of anhydrous sodium acetate was heated at 230–240 °C for 2 h in a stream of nitrogen. The reaction mixture was cooled and dissolved in boiling 95% ethanol. When the mixture cooled, there was obtained 90 g of crystalline material, mp 170–173 °C. Recrystallization from 95% ethanol gave 88.6 g (0.293 mol, 80%) of 7 as slender yellow needles: mp 174–176 °C; IR 981, 1073, 1267, 1660, 1765, 1780 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 6.20 (s, 1 H), 7.20–8.00 (m, 8 H). Anal. Calcd for C<sub>15</sub>H<sub>9</sub>BrO<sub>2</sub>: C, 59.82; H, 3.01; Br, 26.53. Found: C, 59.69; H, 2.96; Br, 26.43.

**2-(*p*-Bromophenyl)-3-phenyl-1-indenone (8).** The procedure followed was essentially that of Allen et al.<sup>41</sup> A solution of 75 g (0.48 mol) of bromobenzene in 150 mL of ether and 11.6 g (0.476 mol) of magnesium was used to prepare phenylmagnesium bromide. To the vigorously stirred warm solution was added 28.7 g (0.095 mol) of the phthalide 7 in 800 mL of benzene at a rate which maintained the solution reflux. At the end of the addition, a brown precipitate appeared. After distillation of excess solvent, the red reaction mixture was cooled in ice, and the complex was destroyed by the addition of 15 mL of concentrated H<sub>2</sub>SO<sub>4</sub> in 300 mL of water. The benzene layer was separated, and the aqueous layer was extracted with 200 mL of benzene. The combined benzene solutions were dried (MgSO<sub>4</sub>), and the solvent was removed to afford a dark red oil. An ethereal solution of the oil, on being allowed to stand at 0 °C for 1 week, deposited 14.6 g of crystals. Recrystallization from ether–methylene chloride gave the product: 13.5 g (0.037 mol, 39%); IR 1015, 1080, 1185, 1610, 1720 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.06–7.60. Anal. Calcd for C<sub>21</sub>H<sub>13</sub>BrO: C, 69.82; H, 3.62; Br, 22.12. Found: C, 69.77; H, 3.72; Br, 22.17.

**2-(*p*-Bromophenyl)-3-phenylindene (3b).** The method of Martin<sup>42</sup> was modified to obtain 3b. A mixture of 150 g (2.3 mol) of zinc, 26 g (0.06 mol) of mercuric chloride, 10 mL of concentrated HCl, and 250 mL of water was stirred for 15 min. The aqueous solution was decanted, and the amalgamated zinc was covered with 150 mL of 95% ethanol and 60 mL of concentrated HCl. A 10-g (0.028 mol) sample of the indenone 8 was added, and the mixture was heated under reflux for 4 h. The reaction was quenched by the addition of 150 mL of water. The liquid phase was decanted and extracted with portions of methylene chloride (2 × 100 mL). The combined organic extracts were washed with 100 mL of water and dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation gave an orange oil which crystallized on addition of ether and petroleum ether, giving 4.8 g (50%) of crystalline material, mp 142–153 °C; however, TLC (35% ether–petroleum ether) showed two close-running spots (*R*<sub>f</sub> 0.4, 0.6). The NMR has peaks at δ 3.84 (s) and 4.90 (s) in a relative ratio of 4:3, respectively, and at δ 7.07–7.54 (m). A portion (250 mg) of the crude product was applied to a 30 × 4.0 cm column of alumina, slurry packed in hexane. Elution was with hexane, and 50-mL fractions were collected. Fractions 36–40 gave 50 mg of crystals with a melting range of 163–180 °C. VPC (5 ft × 1/8 in. of 5% QF-1 on Diatoport 60/80, 210 °C) showed two equal-size peaks (presumed to be 3b and 10) at 6.0- and 7.0-min retention times. Fractions 41–48 yielded 58 mg of 3b as colorless needles: mp 182–185 °C; IR 705, 828, 1014, 1080, 1600 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 3.84 (s, 2 H), 7.00–7.60 (m, 13 H). Anal. Calcd for C<sub>21</sub>H<sub>15</sub>Br: C, 72.64; H, 4.35; Br, 23.01. Found: C, 72.44; H, 4.29; Br, 22.91.

**2-(*p*-Cyanophenyl)-3-phenylindene (3c).** As in the procedure employed in the preparation of the cyanoindene 1c, 4.1 g (0.012 mol) of the mixture of bromoindenes 3b and 10 from the previous experiment was reacted with 1.9 g (0.021 mol) of cuprous cyanide for 2 h in 10 mL of boiling 1-methyl-2-pyrrolidone. The workup, as described in the synthesis of 1c, gave a brown oil. Addition of petroleum ether to the oil afforded 2.2 g of brown crystals. Recrystallization from ether gave 1.4 g (0.005 mol, 42%) of 3c as colorless needles: mp 214–216 °C; IR 698, 835, 1600, 2225 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 3.88 (s, 2 H), 7.02–7.60 (m, 13 H). Anal. Calcd for C<sub>22</sub>H<sub>15</sub>N: C, 90.07; H, 5.15; N, 4.78. Found: C, 89.96; H, 5.22; N, 4.79.

(40) R. Weiss, "Organic Syntheses", Vol. II, Wiley, New York, 1943, p 61.

(41) C. F. H. Allen, J. W. Gates, Jr., and J. A. Van Allen, *Org. Synth.*, 27, 30 (1947).

(42) E. L. Martin, *Org. React.*, 1, 155 (1942).



**2-(*p*-Cyanophenyl)-3-phenyl-1-indenone (9).** The procedure used in the synthesis of **1c** was repeated with 5.0 g (0.014 mol) of the bromoindenone **8** and 2.3 g (0.025 mol) of cuprous cyanide in 10 mL of 1-methyl-2-pyrrolidone. The workup gave brown crystals, and recrystallization from ether afforded 2.3 g (0.076 mol, 54%) of 2-(*p*-cyanophenyl)-3-phenyl-1-indenone (**9**): mp 147–148 °C; IR 1065, 1080, 1610, 1715, 2230 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.10–7.62 (m). Anal. Calcd for C<sub>22</sub>H<sub>13</sub>NO: C, 85.97; H, 4.26; N, 4.56. Found: C, 86.02; H, 4.56; N, 4.79.

**2-(*p*-Cyanophenyl)-3-phenylindene (3c).** A mixture of zinc (37.5 g, 0.6 mol), mercuric chloride (6.5 g, 0.024 mol), and 60 mL of water was stirred for 10 min and the aqueous solution decanted. The zinc was covered with 40 mL of 95% ethanol and 15 mL of concentrated HCl. The indenone **9** (2.0 g, 0.0065 mol) was reacted as described in the preparation of **3b** and gave upon workup 0.82 g (0.0028 mol, 43%) of a brown oil. The NMR spectrum indicated that indene **3c** was present in the crude product. Chromatography, on a 25 × 4.0 cm column of alumina, of a 200-mg portion of the oil with hexane as the eluting solvent gave 180 mg of crystalline 2-(*p*-cyanophenyl)-3-phenylindene (**3c**), mp 213–215 °C.

**2-Phenyl-3-(*p*-bromophenyl)-1-indenone (11).** The procedure of Allen et al.,<sup>41</sup> as used in the synthesis of **8**, was employed on a mixture of 23.4 g (0.105 mol) of benzylidenephthalide and 0.525 mol of *p*-bromophenylmagnesium bromide [the latter was made by the addition of 123 g (0.525 mol) of *p*-dibromobenzene in 300 mL of ether to 12.8 g (0.525 mol) of magnesium]. The workup, identical with that described in the preparation of **8**, gave a red oil. Addition of 25 mL of ether and petroleum ether to the oil rendered 12.1 g of crude red crystals, mp 167–174 °C. Recrystallization from ether gave **11** as bright orange rods: mp 177–179 °C; yield 10.7 g (0.030 mol, 28.5%); IR 1010, 1070, 1180, 1605, 1710 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 6.95–7.45 (m). Anal. Calcd for C<sub>21</sub>H<sub>13</sub>BrO: C, 69.82; H, 3.62; Br, 22.12. Found: C, 69.85; H, 3.67; Br, 22.33.

**2-Phenyl-3-(*p*-bromophenyl)indene (4b).** Zinc (31.7 g, 0.485 mol), mercuric chloride (5.26 g, 19.4 mmol), concentrated HCl (3 mL), and water (35 mL) were stirred for 15 min, and the aqueous phase was decanted. Addition of the amalgam of 40 mL of 95% ethanol, 15 mL of HCl, and 2.0 g (5.55 mmol) of **11** was followed by a 3-h reflux period. Water (100 mL) was then added and the liquid phase extracted with portions of methylene chloride (2 × 75 mL). After the organic extracts were dried (MgSO<sub>4</sub>), removal of the solvent left a yellow oil. Upon addition of petroleum ether 440 mg of crystals deposited; mp 170–177 °C. TLC (hexane) showed two close-moving spots (*R<sub>f</sub>* 0.5, 0.7). The NMR spectrum has peaks at δ 3.88 (s) and 4.90 (s) in a relative ratio of 1.0:2.0, respectively, and at δ 6.91–7.90 (m). The crystals were applied to a 30 × 4.0 cm column of alumina, slurry packed in hexane. Hexane was used as the eluant, and 50-mL fractions were collected. Fractions 20–28 gave 285 mg of yellow crystals, mp 168–180 °C. The NMR spectrum has peaks at δ 3.86 (s) and 4.90 (s) in a relative ratio of 1:10, respectively, and a multiplet at δ 6.90–7.60. Fractions 30–34 yielded 78 mg of **4b** as colorless needles: mp 163–165 °C; combined yield of crystalline material was 363 mg (1.05 mmol, 18%); IR 690, 933, 1012, 1070, 1600 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 3.86 (s, 2 H), 7.10–7.56 (m, 13 H). Anal. Calcd for C<sub>21</sub>H<sub>13</sub>BrO: C, 72.64; H, 4.35; Br, 23.01. Found: C, 72.75; H, 4.32; Br, 23.12.

**2-Phenyl-3-(*p*-cyanophenyl)indene (4c).** Again, as in the procedure employed in the preparation of **1c**, 283 mg (0.81 mmol) of indene **4b** and **12** were treated for 2 h with 132 mg (1.47 mmol) of cuprous cyanide in 3 mL of 1-methyl-2-pyrrolidone under reflux. Upon workup, as described in the synthesis of **1c**, a brown oil was obtained. Addition of petroleum ether and ether gave, upon cooling to 0 °C, 180 mg of yellow crystals. Recrystallization from 95% ethanol produced 155 mg (0.51 mmol, 65%) of **4c** as colorless plates: mp 137–138 °C; IR 693, 845, 1610, 2230 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 3.90 (s, 2 H), 7.09–7.55 (m, 9 H), and 7.54 (A<sub>2</sub>B<sub>2</sub> q, δ<sub>A</sub> 7.44, δ<sub>B</sub> 7.64, *J<sub>AB</sub>* = 8.0 Hz, 4 H). Anal. Calcd for C<sub>22</sub>H<sub>13</sub>N: C, 90.17; H, 5.15; N, 4.78. Found: C, 90.47; H, 4.94; N, 4.88.

***p*-Methoxy-3-benzylidenephthalide (13).** As described previously for the preparation of **7**, a mixture of 18.6 g (0.125 mol) of phthalic anhydride, 25.0 g (0.150 mol) of (*p*-methoxyphenyl)acetic acid and 0.50 g (0.006 mol) of anhydrous sodium acetate was heated to give a yellow oil upon workup. Dissolution of the oil in hot 95% ethanol gave 16.5 g (0.066 mol, 52%) of **13** as bright yellow needles: mp 147–148.5 °C; IR 985, 1177, 1266,

1600, 1760, 1775 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 3.81 (s, 3 H), 6.29 (s, 1 H), 6.74–7.98 (m, 8 H). Anal. Calcd for C<sub>16</sub>H<sub>12</sub>O<sub>3</sub>: C, 76.18; H, 4.80. Found: C, 75.87; H, 4.68.

**2-(*p*-Methoxyphenyl)-3-phenyl-1-indenone (14).** Phenylmagnesium bromide was prepared from 42.4 g (0.270 mol) of bromobenzene in 60 mL of ether by adding the solution to 6.56 g (0.270 mol) of magnesium so that the solution was maintained at the reflux temperature. The mixture was then heated under reflux for 20 min, and a solution of 0.215 g (0.050 mol) of the phthalide **13** in 400 mL of benzene was slowly added so as to maintain the reflux. The workup as described in the synthesis of **8** gave a red oil. Trituration with ether–petroleum ether gave 5.9 g of red crystals, mp 100–115 °C. Recrystallization from ether–methylene chloride yielded 2.2 g (0.007 mol, 14%) of **14** as red needles: mp 118–119.5 °C; IR 1028, 1175, 1245, 1605, 1710, 2845, 2940, 2960 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 3.73 (s, 3 H), 6.60–7.60 (m, 13 H). Anal. Calcd for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>: C, 84.59; H, 5.16. Found: C, 84.54; H, 4.98.

**2-(*p*-Methoxyphenyl)-3-phenylindene (3d).** The method of Martin,<sup>42</sup> described previously for the preparation of **3b**, was employed on 5.0 g (16.0 mmol) of the indenone **13**. A mixture of 88 g (1.35 mol) of zinc, 15.2 g (0.056 mol) of mercuric chloride, 6 mL of concentrated HCl, and 140 mL of water was utilized to form the amalgam. Upon workup, 1.1 g (3.7 mmol) of crude crystalline material was obtained, mp 160–170 °C. TLC (hexane) showed two major spots with approximately the same *R<sub>f</sub>* value of 0.3 and two minor spots (*R<sub>f</sub>* 0.1, 0.7). This crude material was treated with 30 mL of pyridine and 5 mL of dimethylamine for 12 h at room temperature. Water (25 mL) and benzene (25 mL) were added, and the organic layer was separated and washed with 25 mL of 3 N H<sub>2</sub>SO<sub>4</sub> and with 15 mL of water. After the mixture was dried (Na<sub>2</sub>SO<sub>4</sub>), evaporation of solvent yielded 0.93 g of reddish crystals. Chromatography on a 25 × 2.5 cm column of alumina, slurry packed in hexane, and with hexane eluant gave 0.90 g (3.0 mmol, 19%) of **3d** as colorless needles: mp 124–126 °C (lit.<sup>43</sup> mp 123 °C); IR 698, 830, 1032, 1182, 1255, 1605, 2840, 2920, 2940, 2960 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 3.69 (s, 3 H), 3.81 (s, 2 H), 6.68 and 7.09 (AA'BB', 4 H, *J<sub>AB</sub>* = 9.0 Hz), 7.16–7.45 (m, 9 H). Anal. Calcd for C<sub>22</sub>H<sub>18</sub>O: C, 88.56; H, 6.08. Found: C, 88.42; H, 5.93.

**2-Phenyl-3-(*p*-methoxyphenyl)-1-indenone (15).** The *p*-methoxyphenylmagnesium bromide was prepared from 100 g (0.535 mol) of *p*-methoxybromobenzene in 200 mL of ether and 13.0 g (0.535 mol) of magnesium. A solution of 26.5 g (0.120 mol) of benzylidenephthalide in 800 mL of benzene was slowly added with stirring to the warm Grignard reagent so as to maintain the reflux temperature. A red oil resulted upon workup. Trituration with ether–petroleum ether yielded 16.0 g of red crystals, mp 80–120 °C. Recrystallization from ether–hexane gave 14.4 g (0.046 mol, 38%) of **15** as clusters of red needles: mp 121.5–123.0 °C; IR 1030, 1175, 1250, 1605, 1710, 2845, 2940, 2965 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 3.81 (s, 3 H), 6.83–7.58 (m, 13 H). Anal. Calcd for C<sub>22</sub>H<sub>16</sub>O<sub>2</sub>: C, 84.59; H, 5.16. Found: C, 84.58; H, 4.96.

**2-Phenyl-3-(*p*-methoxyphenyl)indene (4d).** The Huang–Minlon modification of the Wolff–Kishner reduction was utilized in the preparation of **4d**. The indenone **15** (8.0 g, 0.026 mol), 125 mL of ethylene glycol, 2.7 mL (0.052 mol) of 99% hydrazine hydrate, and 4.3 g (0.078 mol) of potassium hydroxide were maintained at the reflux temperature for 4 h. The mixture was cooled to 10 °C and extracted with portions of ether (3 × 150 mL). The ethereal extracts were washed with 50 mL of water and dried (Na<sub>2</sub>SO<sub>4</sub>), and the ether was evaporated to give a dark oil. The oil was dissolved in 10 mL of 1-methyl-2-pyrrolidone and the solution heated at reflux under nitrogen for 3 h. After cooling, the solution was extracted with fractions of benzene (2 × 100 mL), and the combined benzene layers were washed with 50 mL of water and dried (Na<sub>2</sub>O<sub>4</sub>). Evaporation of solvent gave 2.4 g of yellow crystals, mp 108–110 °C. Chromatography on a 35 × 2.5 cm column of alumina, slurry packed in and eluted with hexane, yielded 2.1 g (0.007 mol, 27%) of the indene **4d** as colorless needles: mp 115–116 °C; IR 700, 838, 1040, 1175, 1246, 1610, 2830, 2900, 2930, 2950 cm<sup>-1</sup>; <sup>1</sup>H NMR 3.78 (s, 3 H), 3.83 (s, 2 H), 6.90 (d, part

(43) H. P. Kraemer and H. Plieninger, *Tetrahedron*, **34**, 891 (1978). The NMR spectrum of Dr. Plieninger's material was identical with our spectrum. We thank Dr. Plieninger for sending us a sample and a spectrum.

of AA'BB', 2 H,  $J = 9.0$  Hz), 7.49 (m, 11 H). Anal. Calcd for  $C_{22}H_{18}O$ : C, 88.56; H, 6.08. Found: C, 88.38; H, 6.16.

**Irradiations and Thermolysis Reactions. Analysis of Products.** Irradiations were performed with the Hanovia Type L 450-W lamp in a water-cooled quartz immersion well. The apparatus is described elsewhere.<sup>44</sup> In a typical experiment, 49 mg (0.143 mmol) of 1-(*p*-bromophenyl)-1-phenylindene (**1b**) in hexane (300 mL) was irradiated under argon. Aliquots were removed at 1-min intervals and examined by NMR. This was done to avoid undue irradiation and subsequent dimerization of the products. After 3 min the irradiation was terminated, and the hexane was removed under vacuum. The residue was treated with dimethylamine (0.5 mL) in pyridine. The NMR spectrum of the crude residue obtained on removal of these solvents showed two singlets (in  $CDCl_3$ ) due to the methylene groups of **3b** and **4b**. The ratio of these products was determined by running NMR spectra of standard mixtures. The major product, **3b**, was isolated in 76% yield (mp 181–183 °C) by crystallization from petroleum ether. In control experiments, irradiation of the products **3b** and **4b** showed that while slow dimerization occurred, the two products did not interconvert.

Irradiation of 1-(*p*-cyanophenyl)-1-phenylindene (**1c**) was conducted similarly. A 200-mg sample (0.68 mmol) of **1c** in 400 mL of hexane or *tert*-butyl alcohol was irradiated for 11 min. VPC analysis (5 ft  $\times$  1/4 in. of SE-30 at 220 °C) showed 75% reaction of **1c**. Evaporation of solvent and addition of petroleum ether to the residue gave 116 mg (59%) of **3c**, mp 208–212 °C. Recrystallization afforded 110 mg of **3c** (mp 214–216 °C) identical with synthetic 2-(*p*-cyanophenyl)-3-phenylindene. Treatment of the combined mother liquors with dimethylamine (0.5 mL) in pyridine (3.0 mL) on evaporation gave a mixture of reactant **1c** and product **3c**. The phenyl-migrated product, 3-(*p*-cyanophenyl)-2-phenylindene (**4c**) was not observed by NMR in  $CDCl_3$  in either the original mother liquor or in the mixture obtained after equilibration with dimethylamine. Similarly, VPC analysis showed less than 2% of the possible minor product **4c**. Irradiation of products **3c** and **4c** showed that they did not interconvert under the reaction conditions, although slow dimerization appeared to take place.

Irradiation of 1-(*p*-methoxyphenyl)-1-phenylindene (**1d**) utilized 99 mg (0.332 mmol) of **1d** in 200 mL of hexane and a 150-W Hanovia lamp. After 37 min of irradiation the solvent was removed, and the residue was treated with dimethylamine (1.0 mL) in pyridine (6.0 mL). Addition of petroleum ether to the mixture gave 40 mg of **3d** (mp 123–125 °C) identical with an authentic sample of 2-(*p*-methoxyphenyl)-3-phenylindene. NMR analysis of the mother liquors from the crystallization was used to obtain the ratio of **3d** to **4d**, the result of which is given in Table I.

As with the bromo and cyano compounds, the rearrangement products were shown to be stable to irradiation.

**Acetophenone-Sensitized Irradiation of 1-(*p*-Bromophenyl)-1-phenylindene (**1b**).** A solution of 200 mg (0.575 mmol) of 1-(*p*-bromophenyl)-1-phenylindene (**1b**) and 2.0 g (0.0147 mol) of acetophenone in 400 mL of hexane was photolyzed (Pyrex filter) for 18 min. Aliquots were withdrawn at 10 and 18 min. The acetophenone and solvent were distilled, and the aliquots were analyzed by NMR. Each aliquot showed peaks at  $\delta$  3.84 (s) and 3.86 (s) (constant ratio of 2.6:1.0, respectively), 4.87 (br s), 6.67 (AB q), and 6.95–7.62 (m). The reaction was stopped after 18 min, and the solvent and acetophenone were removed by distillation under vacuum. Addition of petroleum ether to the residue gave 33 mg (0.096 mmol, 17%) of crystals (mp 180–182 °C) identical with authentic 2-(*p*-bromophenyl)-3-phenylindene (**3b**). The filtrate was treated with pyridine (6.0 mL) and dimethylamine (1.0 mL) as described previously to give a light brown oil. Chromatography on an 11  $\times$  2.5 cm column of alumina, slurry-packed in and eluted with hexane, gave 160 mg (0.461 mmol) of crystalline material. From the amount of isolated product **3b** and NMR analysis of the mother liquors, the following ratio of products and reactant was obtained: 1-(*p*-bromophenyl)-1-phenylindene (**1b**), 0.203 mmol (35%); 2-(*p*-bromophenyl)-3-phenylindene (**3b**), 0.255 mmol (44.5%); 2-phenyl-3-

(*p*-bromophenyl)-indene (**4b**), 0.099 mmol (17%).

Acetophenone-sensitized reaction of 1-(*p*-cyanophenyl)-1-phenylindene was conducted similarly, and the result is given in Table I.

**Irradiation of 1-(*p*-Bromophenyl)-1-phenylindene and 1-(*p*-Cyanophenyl)-1-phenylindene at Elevated Temperatures.** A solution of 1-(*p*-bromophenyl)-1-phenylindene (50 mg, 0.143 mmol) in decalin (150 mL) was heated to 130 °C and irradiated for 5 min in the Hanovia apparatus with a 150-W, high-pressure mercury arc. Solvent was removed by vacuum distillation and the residue taken up in  $CDCl_3$  and examined by NMR. Two control experiments were also performed: (i) a similar solution was heated to 130 °C for 5 min in the absence of light; (ii) a similar solution was irradiated for 5 min at ambient temperature. No product formation was observed at 130 °C in the absence of light, and the product ratios were found to be identical upon irradiation at 130 °C and at room temperature.

Similar experiments were performed by using a solution of 1-(*p*-cyanophenyl)-1-phenylindene (50 mg) in decalin (150 mL).

**Thermal Reactions. Thermolysis of 1-(*p*-Bromophenyl)-1-phenylindene (**1b**).** A solution of 42 mg of **1b** in 2.5 mL of diphenyl ether was heated at the reflux temperature (258 °C) under nitrogen for 24 h. The diphenyl ether was removed by vacuum distillation, leaving a crystalline residue (42 mg) which shows the following NMR absorption: singlets at  $\delta$  3.84 and 3.86 (relative ratio of 1.08:1.00), multiplet at  $\delta$  7.00–7.60. The NMR of standard mixtures of products, by use of the singlet signals of methylene protons at  $\delta$  3.84 and 3.86, indicated the presence in the reaction mixture of 52% of 2-(*p*-bromophenyl)-3-phenylindene (**3b**) and 48% of 2-phenyl-3-(*p*-bromophenyl)indene (**4b**). Addition of petroleum ether to the crystals yielded 17 mg (40%) of 2-(*p*-bromophenyl)-3-phenylindene (**3b**), mp 181–183 °C.

In a similar experiment 75 mg of 1-(*p*-cyanophenyl)-1-phenylindene was heated under reflux in diphenyl ether (2.5 mL), and the products were analyzed as in the above irradiations. The two products **3c** and **4c** were formed in the ratio 82:18. Thermolysis of 1-(*p*-methoxyphenyl)-1-phenylindene was conducted similarly. Results for all these compounds are given in Table I.

**Quantum Yield Measurements. Materials.** All solvents, sensitizers, quenchers, and other reagents were distilled or crystallized before use. Hexane (reagent grade) was purified by being stirred with fuming  $H_2SO_4$  for 24 h, followed by successive washings with water, 10% aqueous sodium bicarbonate, and water. After the mixture was dried ( $Na_2SO_4$ ), the fraction boiling at 66–67 °C was collected. This solvent had no absorption above 210 nm. 4,4'-Dichlorobenzophenone was prepared by reaction of chlorobenzene with carbon tetrachloride and hydrolysis of the resulting diaryldichloromethane.<sup>45</sup> Actinometry was by the ferrioxalate method of Hatchard and Parker.<sup>46</sup>

**Procedures for 1,1-Diphenylindene Reaction.** The results of Tables II, IV, and V were obtained, in most cases, by using the monochromator, beam splitter, and optical bench described previously.<sup>47</sup> Irradiation was at 275 nm in the direct irradiation and at 370 nm in the sensitization. Assay of products was by VPC on 5 ft  $\times$  0.25 in. of QF-1 on 60–70-mesh Chromosorb W at 180 °C with helium at 40 mL/min as the carrier gas. *p*-Terphenyl was used as internal standard.

**Correction for Light Absorbed by Products.** Since the products absorb strongly at the wavelengths used, corrections for this were applied in all cases. In the direct irradiation, the rate of product (P) appearance [equal to rate of reactant (R) disappearance] is given by eq 4 or 5, where P is product, R is reactant,

$$d[P]/dt = d[R]/dt = (\text{quantum yield}) \times (\text{rate of light absorption by reactant}) \quad (4)$$

$$\frac{d[P]}{dt} = \frac{-d[R]}{dt} = \frac{\epsilon_P[R]}{\epsilon_R[R] + \epsilon_P[P]} \Phi I \quad (5)$$

(45) J. F. Norris and W. C. Twieg, *Am. Chem. J.*, **30**, 392 (1903).

(46) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London., Ser. A*, **235**, 518 (1956).

(47) R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *J. Am. Chem. Soc.*, **96**, 692 (1974).

(44) See, for example, *Org. Photochem. Synth.*, **1**, 13–15 (1971).

$\epsilon_P$  and  $\epsilon_R$  are the extinction coefficients of P and R, respectively,  $\Phi$  is the quantum yield, and  $I$  is the light intensity. Equation 5 can be integrated to give<sup>3</sup> eq 6. If [P] is the amount of product

$$([R_0] - [R_t])(1 - \epsilon_P/\epsilon_R) + (\epsilon_P/\epsilon_R)[R_0] \ln [R_0]/[R_t] = \Phi I t \quad (6)$$

at time  $t$ , eq 6 gives eq 7, from which  $\Phi$  can be calculated.

$$\Phi I t = (1 - \epsilon_P/\epsilon_R)[P] + \epsilon_P/\epsilon_R[R_0] \ln [R_0]/[R_0] - [P] \quad (7)$$

In the sensitized reactions, product (P) competes with sensitizer (S) for the incident light. The equation is given by eq 8, where

$$\frac{d[P]}{dt} = \frac{\epsilon_S[S]}{\epsilon_S[S] + \epsilon_P[P]} \Phi I \quad (8)$$

$\epsilon_S$  and [S] are the extinction coefficient and concentration of sensitizer, respectively. This equation gives eq 9, where [P]<sub>t</sub> is the product concentration at time  $t$ .

$$\Phi I t = [P_t] + \epsilon_P[P_t]^2/2\epsilon_S[S] \quad (9)$$

Additionally, quantum yields given for the sensitized reactions have been corrected for inefficiency in energy transfer to the substrate.

The following ultraviolet absorption data was used. 1,1-Diphenylindene:  $\lambda_{\max}$  (hexane) 260, 275 nm;  $\log \epsilon$  3.72, 3.65. 2,3-Diphenylindene:  $\lambda_{\max}$  (hexane) 237, 305 nm;  $\log \epsilon$  4.30, 4.26;  $\log \epsilon$  at 275 nm = 3.87. 1,2-Diphenylindene:  $\lambda_{\max}$  (hexane) 237, 305 nm;  $\log \epsilon$  4.11, 4.28;  $\log \epsilon$  at 275 nm = 3.78. 1-(*p*-Cyanophenyl)-1-phenylindene: inflections (EtOH) at  $\lambda$  243, 265 nm;  $\log \epsilon$  4.33, 3.93;  $\log \epsilon$  at 275 nm = 3.83;  $\log \epsilon$  at 275 nm = 3.84. 2-(*p*-Cyanophenyl)-3-phenylindene:  $\lambda_{\max}$  (EtOH) 240, 330 nm;  $\log \epsilon$  4.31, 4.39;  $\log \epsilon$  at 275 nm = 3.65. 4,4'-Dichlorobenzophenone:  $\lambda_{\max}$  (EtOH) 345 nm;  $\log \epsilon$  at 2.30;  $\log \epsilon$  at 370 nm = 1.90.

**Quantum Yields of 1-(*p*-Cyanophenyl)-1-phenylindene.** <sup>14</sup>C Isotope Dilution Experiments. Synthesis of <sup>14</sup>C-Labeled 1-(*p*-Cyanophenyl)-1-phenylindene. Cuprous cyanide of activity 132.98  $\mu$ Ci/mmol was prepared by the standard method.<sup>48</sup> Labeled cuprous cyanide (335.9 mg, 1.88 mmol) and 1-(*p*-bromophenyl)-1-phenylindene (700.7 mg, 2.01 mmol) were heated under reflux in dimethylformamide under nitrogen for 6 h. Workup as described above gave 410 mg of solid which was a mixture of 1b and 1c. The reflux in dimethylformamide was repeated with this solid and 300 mg of unlabeled cuprous cyanide. After 24 h of reflux and aqueous workup, 230 mg of <sup>14</sup>C-labeled 1-(*p*-cyanophenyl)-1-phenylindene, 1c-<sup>14</sup>CN, was obtained; mp 153–155 °C (from 95% EtOH). The specific activity was 27.17  $\mu$ Ci/mmol, which was unchanged on further crystallization.

**Quantum Yields of 1c. (a) Direct Irradiation.** The solution (26 mL) of 1c-<sup>14</sup>CN in absolute ethanol, was IR-radiated by using the monochromator, and the light absorbed was determined by ferrioxalate actinometry. Either 3c or 4c was added as a "cold" carrier, and the ethanol was removed. The residue was stirred (12 h) under nitrogen with 5.0 mL of pyridine and 1.0 mL of dimethylamine. The <sup>14</sup>C-labeled product (3c or 4c) was isolated by extraction with 2 N H<sub>2</sub>SO<sub>4</sub> and ether and was crystallized (EtOH) to constant activity. The activity was measured by liquid-scintillation counting on a Nuclear Chicago Mark I liquid-scintillation counter with "Aquasol" (New England Nuclear) as the fluor. In one experiment (run 2, Table II) incomplete exclusion of oxygen during workup led to oxidation of the indene product to indenone. The latter was isolated by chromatography on silica gel, eluted with benzene-hexane (1:1), and reduced with sodium borohydride to give the indenol which was used for scintillation counting.

**(b) Sensitized Irradiations.** Solutions (26 mL) of 1c-<sup>14</sup>CN and either acetophenone or 4,4'-dichlorobenzophenone in benzene were irradiated at 370 nm by using the monochromator. After workup (as described above), the required product (3c or 4c) was isolated by column chromatography (silica gel, eluted with 1:1 benzene-hexane) and was crystallized to constant activity. The

results of all these experiments are given below and in Table II.

**Run 1:** <sup>14</sup>CN-labeled 1-(*p*-cyanophenyl)-1-phenylindene (1c); 36.8  $\mu$ mol, activity 27.19  $\mu$ Ci/mmol; irradiated at 275 nm with  $2.09 \times 10^{-2}$  meinstein; crude product diluted with 79.4 mg (0.27 mmol) of 2-(*p*-cyanophenyl)-3-phenylindene.

After chromatographic separation, recrystallization to constant activity (EtOH) gave a final product (mp 214–216 °C) containing 0.814  $\mu$ Ci/mmol, corresponding to a quantum yield of 0.43 mol/einstein.

**Run 2.** This was identical to run 1 except that product was assayed as the 1-indanol. After initial purification by column chromatography, the indenone (mp 145–147 °C) was recrystallized to constant activity. The final product contained 0.970  $\mu$ Ci/mmol, corresponding to a quantum yield of 0.48 mol/einstein.

**Run 3.** Compound 1c (32.23 mg, 0.11 mmol; activity 27.19  $\mu$ Ci/mmol) and 4,4'-dichlorobenzophenone ( $5.03 \times 10^{-2}$  M) in benzene were irradiated at 370 nm with  $7.93 \times 10^{-2}$  meinstein. The crude product was diluted with 65.7 mg (0.22 mmol) of 2-(*p*-cyanophenyl)-3-phenylindene. Recrystallization to constant activity gave a final product with a melting point of mp 215–217 °C and an activity of 0.622  $\mu$ Ci/mmol, corresponding to a quantum yield of 0.51.

**Run 4.** Compound 1c (32.23 mg, 0.11 mmol; activity 27.19  $\mu$ Ci/mmol) and acetophenone ( $4.42 \times 10^{-2}$  M) in benzene were irradiated at 270 nm with  $5.77 \times 10^{-2}$  meinstein. The crude product was diluted with 81.3 mg (0.27 mmol) of 2-(*p*-cyanophenyl)-3-phenylindene. Recrystallization to constant activity gave a final product with a melting point of 215–217 °C and an activity of 0.074  $\mu$ Ci/mmol, corresponding to a quantum yield of 0.55 mol/einstein.

**Run 5.** Compound 1c (8.99 mg, 0.03 mmol; activity 27.19  $\mu$ Ci/mmol) was irradiated at 275 nm with  $2.06 \times 10^{-2}$  meinstein. The crude product was diluted with 76.3 mg (0.26 mmol) of 3-(*p*-cyanophenyl)-2-phenylindene. Recrystallization to constant activity gave a final product containing  $\leq 2.7 \times 10^{-3}$   $\mu$ Ci/mmol, corresponding to a quantum yield of <0.001 mol/einstein.

**Run 6.** Compound 1c (32.23 mg, 0.11 mmol; activity 27.19  $\mu$ Ci/mmol) and 4,4'-dichlorobenzophenone ( $5.03 \times 10^{-2}$  M) in benzene were irradiated at 370 nm with  $3.86 \times 10^{-2}$  meinstein. The crude product was diluted with 3-(*p*-cyanophenyl)-2-phenylindene (59.9 mg, 0.20 mmol). Recrystallization to constant activity gave a final product containing  $\leq 6.2 \times 10^{-3}$   $\mu$ Ci/mmol, corresponding to a quantum yield of  $\leq 0.001$  mol/einstein.

**Spectroscopy.** Fluorescence and phosphorescence spectra were measured with the Aminco-Bowman spectrofluorimeter using a Dewar and rotating shutter phosphoroscope attachment for the long-lived phosphorescence.

**Thermolysis of 1-(*p*-Bromophenyl)-1-phenylindene and 1-(*p*-Cyanophenyl)-1-phenylindene Kinetics.** The rates of rearrangement of 1b and 1c were measured by the technique of Miller et al.<sup>7</sup> Samples of the indene were dissolved in diphenyl ether containing a known amount of toluene, and the solutions were sealed under vacuum in NMR tubes. The tubes were heated at 280 °C in a silicone oil bath. Tubes were removed from the oil bath one at a time, after different times. The amount of product in each tube was then determined by comparing the areas of the methylene singlets of the products (3b or 3c) with that of the toluene methyl group. Good first-order plots were obtained, giving rate constants of  $0.7 \times 10^{-4}$  s<sup>-1</sup> for 1b and  $18 \times 10^{-4}$  s<sup>-1</sup> for 1c.

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**Registry No.** 1a, 18636-52-7; 1b, 52033-61-1; 1c, 52033-62-2; 1c-<sup>14</sup>CN, 75948-87-7; 1d, 52033-63-3; 3b, 52033-64-4; 3c, 52033-65-5; 3d, 52033-66-6; 4b, 52033-67-7; 4c, 52033-68-8; 4d, 52033-69-9; 5, 75948-

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88-8; 6, 75961-47-6; 7, 75948-89-9; 8, 3312-37-6; 9, 13304-43-3; 10, 52033-64-4; 11, 42349-44-0; 12, 75948-90-2; 13, 7434-84-6; 14, 3312-38-7; 15, 17932-18-2; 2,3-diphenylindene, 5324-00-5; 1,2-diphenylindene, 18636-54-9; 1,1-dimethylindene, 18636-55-0; 3-(*p*-bromophenyl)-3-phenyl-1-indanol, 75948-91-3; 1-(*p*-bromophenyl)-1,1-diphenylcarbinol, 61623-62-9; PhBr, 108-86-1; *p*-bromobenzophenone,

90-90-4; malonic acid, 141-82-2; phthalic anhydride, 85-44-9; (*p*-bromophenyl)acetic acid, 1878-68-8; benzylidenephthalide, 4767-55-9; *p*-BrC<sub>6</sub>H<sub>4</sub>Br, 106-37-6; (*p*-methoxyphenyl)acetic acid, 104-01-8; *p*-methoxybromobenzene, 104-92-7; methylcyclopentadiene, 96-38-8; vinylcyclopentadiene, 29647-85-6; formylcyclopentadiene, 56598-51-7; phenylcyclopentadiene, 1961-98-4.

## Solvomercuration-Demercuration. 9. Oxymercuration-Demercuration of Chloro-, Epoxy-, and Thiomethyl-Substituted Alkenes

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The oxymercuration-demercuration (OM-DM) of allyl, crotyl, 3-buten-1-yl, 4-penten-1-yl, and 5-hexen-1-yl chlorides and methyl sulfides as well as 3,4-epoxy-1-butene, 4,5-epoxy-1-pentene, and 5,6-epoxy-1-hexene has been studied. Allyl chloride undergoes a slow but normal OM to give the Markovnikov oxymercuration. However, in situ demercuration under the standard conditions (NaOH, NaBH<sub>4</sub>) gives only allyl alcohol. Fortunately, demercuration with an ethanolic solution of sodium borohydride results in high yields of the chlorohydrin accompanied by small amounts of propylene oxide. In contrast, crotyl chloride fails to give any products resulting from the OM-DM sequence. Thus, 3-buten-2-yl chloride underwent only solvolytic reaction while 2-methylallyl chloride underwent exclusive OM to give, upon DM, the expected Markovnikov chlorohydrin. Similarly, 3-buten-1-yl chloride underwent exclusive hydration under the standard OM-DM conditions. In the case of 4-penten-1-yl chloride, the C1-C5 neighboring-group participation was seen during OM. However, 5-hexen-1-yl chloride showed exclusive hydration to give a 94% yield of the Markovnikov chlorohydrin. The approximate rates of solvolysis of a series of representative alkyl halides have been determined under the OM conditions. The OM-DM of 3,4-epoxy-1-butene proceeded to give hydrated products although the yield was low, ca. 60%. On the other hand, 4,5-epoxy-2-pentene gave products arising only from participation of the epoxide ring in the OM stage. Moreover, the yields of these products are very low, only ca. 15%. By contrast, the OM-DM of 4,5-epoxy-1-pentene proceeds cleanly, giving a 96% yield of the Markovnikov epoxy alcohol. In the case of 5,6-epoxy-1-hexene, ~80% of the products arise from epoxide participation in the OM stage. With the exception of the crotyl derivative, the (methylthio)alkenes undergo hydration cleanly, although slowly, to give approximately 70-80% yields of the thio alcohols. The crotyl alkene gave 3-buten-2-ol in only ~20% yield.

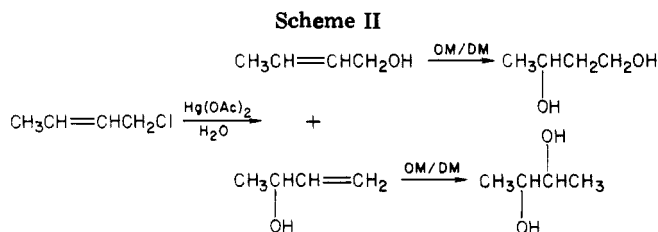
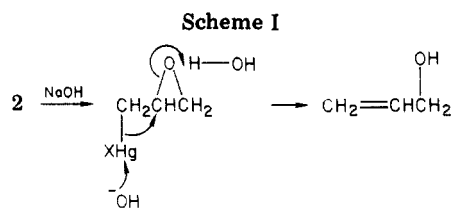
In the preceding paper,<sup>2</sup> it was demonstrated that the methoxy, hydroxy, and acetoxy groups in general offered no major difficulties in the oxymercuration-demercuration sequence. Consequently, it appeared appropriate to expand our studies on the OM-DM of representative substituted alkenes. Thus, we examined the chloro, epoxy, and methylthio groups in the allyl, crotyl, 3-buten-1-yl, 4-penten-1-yl, and 5-hexen-1-yl structures.

For various reasons, each of these groups might be expected to pose difficulties, especially during the OM stage. For example, it is well-known that mercury salts catalyze the solvolyses of alkyl halides.<sup>3</sup> Similarly, organosulfur compounds often react readily with mercuric salts to form stable addition compounds.<sup>4</sup> It is shown that certain epoxides are incompatible with the oxymercuration reaction.<sup>5,6</sup>

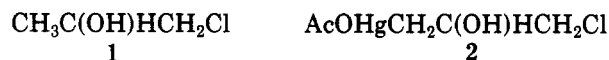
### Results and Discussion

**Chloro-Substituted Alkenes.** The significant results for the OM-DM of these alkenes are summarized in Table I.

The oxymercuration of allyl chloride is unusually sluggish, requiring 1 h to achieve an approximately 90% con-



version of the olefin. However, in situ demercuration under standard conditions (addition of excess sodium hydroxide followed by the addition of an alkaline solution of sodium borohydride) results in an 83% yield of allyl alcohol, rather than the expected Markovnikov chlorohydrin 1. However, <sup>1</sup>H NMR analysis of the OM reaction



mixture indicates that the expected oxymercuration 2 is formed in high yield. Subsequent experiments reveal that the mercurial 2, upon treatment with base, is rapidly converted to allyl alcohol. A reasonable mechanism for this transformation is outlined in Scheme I.<sup>7</sup>

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