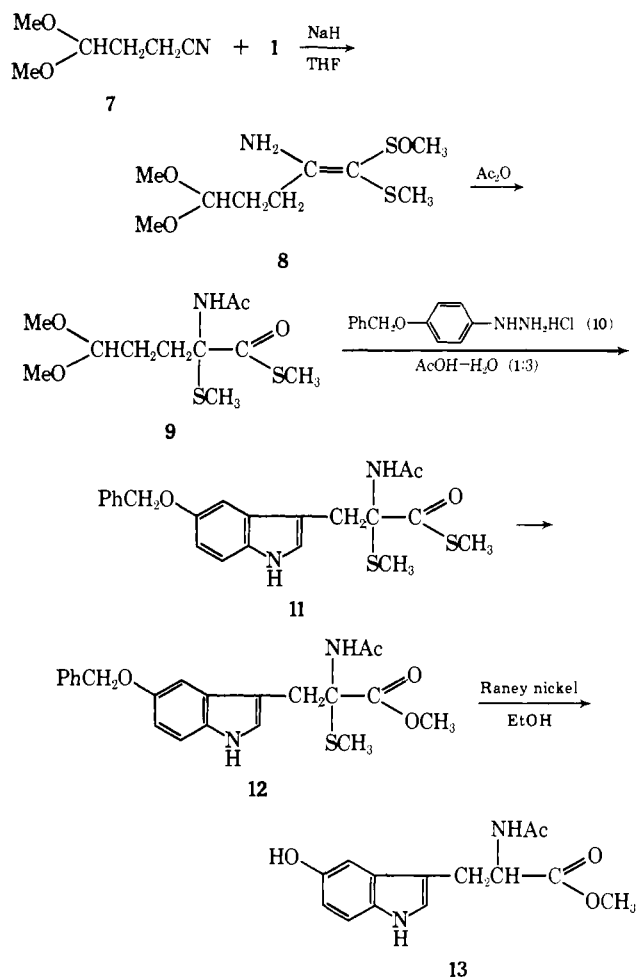


## Scheme IV



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### Sigmatropic Rearrangements of 1,1-Diarylimindenes. Migratory Aptitudes in Ground and Excited States

Sir:

Migratory aptitudes of substituted aryl groups in reactive intermediates have been used to determine the transition state structure for the migration.<sup>1-6</sup> 1,2-Phenyl shifts in 1,1-diphenylimindene can be induced by

(1) Accounts may be found in (a) G. W. Wheland, "Advanced Organic Chemistry," Wiley, New York, N. Y., 3rd ed, 1960, p 573-597; (b) Y. Pocker in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 22.

(2) C. Ruckardt and R. Hecht, *Ber.*, **98**, 2471 (1965).

(3) H. E. Zimmerman and J. H. Munch, *J. Amer. Chem. Soc.*, **90**, 187 (1968).

(4) (a) H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *J. Amer. Chem. Soc.*, **87**, 1138 (1965); (b) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967); (c) H. E. Zimmerman and N. Lewin, *ibid.*, **91**, 879 (1969).

(5) S. S. Hixson, *J. Amer. Chem. Soc.*, **94**, 2307 (1972).

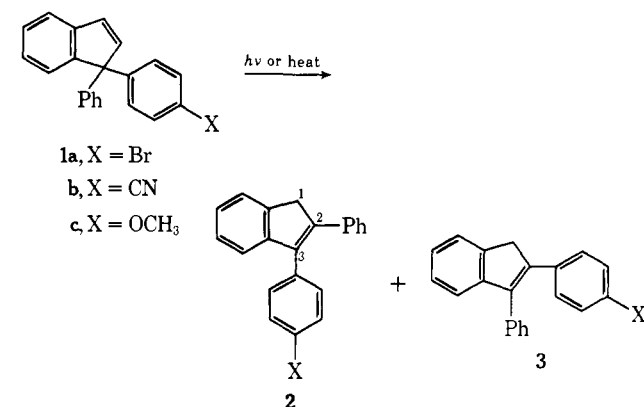
(6) (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klöse, *J. Amer. Chem. Soc.*, **87**, 1410 (1965); (b) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

heating<sup>7,8</sup> or by ultraviolet irradiation,<sup>6b,9</sup> and this structure therefore provided an attractive opportunity to compare aryl group migratory aptitudes in the ground and excited states. We report here the results of such a study.

The 1,1-diarylimindenes used were 1-(*p*-bromophenyl)-1-phenylimindene (**1a**), 1-(*p*-cyanophenyl)-1-phenylimindene (**1b**), and 1-(*p*-methoxyphenyl)-1-phenylimindene (**1c**). The bromo compound **1a** was synthesized from 3-(*p*-bromophenyl)-3,3-diphenylpropionic acid, as described for 1,1-diphenylimindene.<sup>9,10</sup> The *p*-cyano and *p*-methoxy compounds were prepared from the bromo derivative by copper-catalyzed displacements.<sup>11,12</sup>

The reactions are shown in Scheme I. The thermal

## Scheme I



reactions<sup>8</sup> were conducted by heating 50-100 mg of the indene in diphenyl ether (2-3 ml) at reflux (258°) under nitrogen for 18-24 hr. Two products were found in each case—the 2,3-diphenylimindene derivatives, **2** and **3**.

The photorearrangements were performed as described previously,<sup>9</sup> using 50-200 mg of the indene in 300-400 ml of solution. Aliquots were withdrawn and analyzed by vpc and nmr. Since two 1,2- and two 2,3-diarylimindene products are formed,<sup>9</sup> the aliquots were treated with diethylamine in pyridine.<sup>13</sup> This converted the 1,2- into the 2,3-isomers,<sup>9</sup> and the ratio of the latter two products<sup>14</sup> was measured.<sup>15</sup> Products were isolated by crystallization and chromatography and identified by comparison with authentic materials.

The results are given in Table I. The striking feature is that the excited-state process is more selective

(7) C. F. Koelsch and P. R. Johnson, *J. Amer. Chem. Soc.*, **65**, 567 (1943).

(8) L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Amer. Chem. Soc.*, **91**, 1578 (1969); L. L. Miller and R. F. Boyer, *ibid.*, **93**, 650 (1971).

(9) J. J. McCullough, *Can. J. Chem.*, **46**, 43 (1968).

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

(11) (a) M. S. Newman and H. Boden, *J. Org. Chem.*, **26**, 2525 (1961); (b) R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1097 (1964); (c) R. G. R. Bacon and S. C. Rennison, *ibid.*, 312 (1969).

(12) All new compounds gave satisfactory analytical figures, gave infrared and nmr spectra consistent with the assigned structures, and gave sharp-melting crystals: **1a** mp 118-119°; **1b** mp 152-154°; and **1c** mp 78-79°.

(13) G. Bergson, *Acta Chem. Scand.*, **17**, 2691 (1963).

(14) The structures of **2** and **3** were established by unambiguous synthesis, using the general route described for 2,3-diphenylimindene.<sup>9</sup> **3a**, **b**, and **c** had melting points of 184-186, 214-216, and 124-126° and **2a**, **b**, and **c** had melting points of 163-165, 139-141, and 115-116°, respectively. These products were stable under the reaction conditions.

(15) Analysis by vpc was conducted on 5 ft × 1/8 in. of 5% QF-1 on Chromosorb W at 200°. Nmr analysis was performed on the HA-100, and the singlet resonances of the methylene groups (which were in the range 3.5-4.0 ppm) were used to determine ratios. Both vpc and nmr figures were checked against standard mixtures of synthetic materials, and results from the two methods were in good agreement.

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

Energy Input	Substituent (-X)	Solvent	% reaction	Ratio <sup>b</sup> 3:2
Ultraviolet (direct)	-CN	Hexane	59	>98:2
	-CN	<i>tert</i> -Butyl <sup>a</sup> alcohol	75	>98:2
Acetophenone sensitization	-Br	Hexane	88	86:14
	-OCH <sub>3</sub>	Hexane	89	95:5
	-CN	<i>tert</i> -Butyl <sup>a</sup> alcohol	62	>98:2
	-Br	Hexane	78	72:28
Heat (258 °)	-CN	Diphenyl ether	100	82:18
	-Br		100	52:48
	-OCH <sub>3</sub>		100	50:50

<sup>a</sup> The same result was obtained with 95% ethanol as solvent.

<sup>b</sup> Estimated maximum analytical error was  $\pm 5\%$ .

(favoring migration of all three *p*-X-phenyl groups in preference to phenyl) than the ground-state process. As far as we are aware, there is no model, based on theory or experiment, which could have been used to predict this result.

A complete discussion is beyond the space limitations of this paper; however, we can make the following points. First, the excited-state process does parallel, at least qualitatively, the results of Hixson<sup>5</sup> on a related reaction in acyclic compounds. Hixson interpreted his results in terms of odd-electron character in the transition state for migration and pointed out that they were consistent with predictions of Hückel calculations.<sup>16</sup> However, an alternative interpretation based on charge-transfer interactions is also reasonable. It is well known that charge transfer is important in excited-state interactions,<sup>17</sup> and recent experimental work has demonstrated this for bimolecular processes.<sup>18</sup> The latter has shown that, in quenching of an excited state, the rate is high if one partner is a good electron donor and the other a good acceptor, and quantitative correlations with reduction, oxidation, and ionization potentials have been made. Similar factors could operate in the interaction between the nonconjugated chromophores in the excited state of **1** to make the substituted group the better migrator (*vs.* phenyl).<sup>19-21</sup>

For ground-state processes, theory predicts charge-transfer interaction to be much less important.<sup>17</sup> The

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

(17) The theoretical basis for this statement was developed by Mulliken; R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York, N. Y., 1969.

(18) (a) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970), and references cited; (b) J. B. Guttenplan and S. G. Cohen, *Tetrahedron Lett.*, 2163 (1972); *J. Amer. Chem. Soc.*, **94**, 4040 (1972); (c) S. Ander, H. Blume, G. Heinrich, and D. Schulte-Frohlinde, *Chem. Commun.*, 745 (1968); (d) D. Schulte-Frohlinde and R. Pfefferkorn, *Ber. Bunsenges. Phys. Chem.*, **72**, 350 (1968); (e) H. S. Samant and A. J. Yarwood, *Can. J. Chem.*, **49**, 2053 (1971).

(19) Electron transfer between the styrene system and substituted aryl group is more favorable energetically in **1b** and **1c**, than it would be for an unsubstituted phenyl group. For example,  $E_{ox}(\text{styrene})^{20} + E_{red}(\text{benzonitrile})^{18a} = 94.4$  kcal;  $E_{red}$  for benzene has not been measured directly on account of its high value, and therefore  $E_{ox}(\text{styrene}) + E_{red}(\text{benzene}) > 94.4$  kcal. Similarly, charge transfer from the *p*-methoxyphenyl group of **1c** to the styrene chromophore should certainly be favored over the corresponding phenyl-styrene interaction.

(20) N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).

(21) Hixson observed solvent incorporation on irradiation in methanol of 1,3-diphenylpropene derivatives (*J. Amer. Chem. Soc.*, **94**, 2505 (1972)). These products are consistent with highly polar intermediates, such as zwitterions, which could be formed by intramolecular electron transfer in the polar solvent.

relatively low selectivity in the thermal migrations could reflect a radical-like transition state. Ruckardt<sup>2</sup> showed that a *p*-cyanophenyl group had a much higher migratory amplitude than other aryl groups, to a free radical center.<sup>22</sup> Our results for the thermal reaction could therefore be consistent with a radical-like process.<sup>23</sup> A full discussion, including the orbital symmetry aspects, will be given in a full paper.

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(22) (a) Ruckardt found that *p*-anisyl migrated more readily than phenyl in one case<sup>22b</sup> and less readily in another.<sup>2</sup> However, the differences between these two aryl groups was small, and *p*-cyanophenyl was by far the best migrator.<sup>2</sup> (b) C. Ruckardt and H. Trautwein, *Ber.*, **96**, 160 (1963).

(23) The *p*-cyanophenyl group does not exert its effect by retarding phenyl migration. The rate constants are (280°, diphenyl ether): 1,1-diphenylindene,  $2.0 \times 10^{-4} \text{ sec}^{-1}$ ; **1a**,  $0.7 \times 10^{-4} \text{ sec}^{-1}$ ; **1b**,  $18 \times 10^{-4} \text{ sec}^{-1}$ .<sup>24</sup>

(24) Personal communication from Dr. L. L. Miller.

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## Evidence for Electron Transfer in the Photoreduction of Aromatic Nitro Compounds

Sir:

Recently, we reported the efficient photoreduction of 4-nitropyridine to 4-hydroxylaminopyridine in 50% isopropyl alcohol-water containing HCl.<sup>1</sup> The enhanced photoreduction of nitrobenzene in the same solvent system has also been demonstrated.<sup>2</sup> The results indicated that protonation effects were important, but whether the primary process involved electron transfer or proton transfer to the  $^3n, \pi^*$  state could not be distinguished. In the enhanced photoreduction of nitrobenzene in HCl solutions,<sup>2</sup> we suggested that protonation in the excited  $^3n, \pi^*$  state may be operative, since the chloride ion alone does not lead to enhanced photoreduction; however, Wubbels, *et al.*,<sup>3</sup> have recently demonstrated that the enhanced photoreduction occurs in HCl but not in H<sub>2</sub>SO<sub>4</sub>. The results were interpreted in terms of an electron transfer from the chloride ion to nitrobenzene in its  $^3n, \pi^*$  state, which is followed by protonation. It is noteworthy that Wubbels, *et al.*,<sup>3</sup> proposed the formation of a charge-transfer complex of the type  $[\text{PhNO}_2^-, \text{Cl}^-]$ , but they were unable to demonstrate the intermediacy of the complex or of the nitrobenzene anion. It is appealing that such a mechanism can be tested by a flash photolysis experiment in which the absorption spectrum of the corresponding anion may be observed. Accordingly, we present the flash photolysis results obtained for nitrobenzene and 4-nitropyridine in aqueous isopropyl alcohol (IPA) solutions containing HCl. The nitrobenzene anion has been reported by Kemula and Sioda<sup>4</sup>

(1) A. Cu and A. C. Testa, *J. Phys. Chem.*, **77**, 1487 (1973).

(2) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **89**, 6917 (1967).

(3) G. G. Wubbels, J. W. Jordan, and N. S. Mills, *J. Amer. Chem. Soc.*, **95**, 1281 (1973).

(4) W. Kemula and R. Sioda, *Nature (London)*, **197**, 588 (1963).