

# Chlorine Atom/Benzene System. 1. The Role of the 6-Chlorocyclohexadienyl Radical

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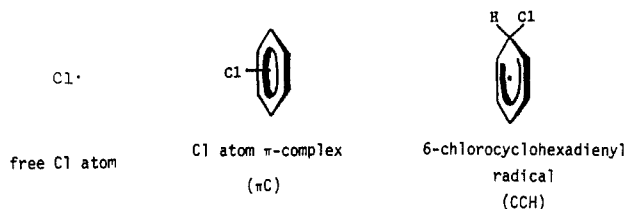
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**Abstract:** The concept of radical reactivity mediated by solvation has rested mainly on the alteration of  $\text{Cl}^\bullet$  properties by aromatic solvents. For this reason, the full scope of the benzene/ $\text{Cl}^\bullet$  system has been reexamined to evaluate the description of that system based largely on a  $\pi$ -complex (solvation). At the present time, the  $\pi$ -complex description rests narrowly on the assignment of a 490-nm absorption, which, even if correct, could not provide an unambiguous structure assignment. Results are presented which describe the selectivities in alkane substitutions as a function of the concentrations of both benzene and the alkane. Selectivities increase with decreasing alkane concentrations, reaching a plateau below 0.1 M alkane. The change in selectivity is the result of variable contributions of both a low- and a high-selectivity intermediate, LSI and HSI, respectively. The observed selectivity at a given  $[\text{PhH}]$  and  $[\text{RH}]$  is the consequence of a unique  $[\text{LSI}]/[\text{HSI}]$  ratio. A range of substrates and their effect on DMB selectivity were studied, and from these results details regarding the chemistry of the HSI were extracted. Several features of the LSI/HSI equilibrating system are realized. (1) Reaction of alkyl radicals with  $\text{Cl}_2$  in benzene produces the LSI, (2) the LSI does not exhibit the characteristics of free chlorine atom, and (3) at alkane concentrations  $\leq 0.1$  M equilibrium between the LSI and HSI is attained. The LSI/HSI equilibrating system is most readily understood if the HSI is assigned to the 6-chlorocyclohexadienyl radical (CCH). It is shown that at fixed  $[\text{PhH}]$  and  $[\text{DMB}]$ , added reagents (T) which react with CCH, such as maleic anhydride (MA) or  $\text{Cl}_2$ , bring about an increase in the LSI/HSI ratio. Low-selectivity hydrogen abstractions (LSI function) are best ascribed to a mixture of chlorine atom and the chlorine atom/benzene  $\pi$ -complex. The chemistry of CCH is as follows: (1) loss of the ipso H to  $\text{O}_2$  yielding  $\text{PhCl}$  and  $\text{HO}_2^\bullet$ , (2) reactions of  $\text{Cl}_2$  or (3) maleic anhydride with the aromatic nucleus of CCH resulting in additions to the ring, (4) the transfer of Cl to alkenes, and (5) the highly selective retardation of rates of reaction with alkanes producing alkyl radicals, HCl, and benzene. The results of a kinetic analysis, accounting for the effect of  $[\text{PhH}]$ ,  $[\text{RH}]$ , and CCH trapping agents (T), are presented. For CCH, the following reactivity order is established: maleic anhydride (6) > *trans*-dichloroethene (5) > 2,3-dimethylbutane (2) > pentane (1) >  $\text{Cl}_2$  [1.00] > neopentane (<0.1). The selectivity of CCH (per H) was found to be  $3^\circ$  (130) >  $2^\circ$  (27) >  $1^\circ$  [1.00]. These properties can be rationalized with canonical structures for CCH wherein spin density at carbon, chlorine, and the ipso hydrogen makes contributions to the hybrid.

## I. Introduction

**A. Overview.** Where chlorine atoms are produced in the presence of benzene, three potential intermediates have been considered in order to explain the resultant chemistry: free chlorine atom ( $\text{Cl}^\bullet$ ), a chlorine atom/benzene  $\pi$ -complex ( $\pi\text{C}$ ), and the 6-chlorocyclohexadienyl radical (CCH).<sup>1</sup> The relationship(s)

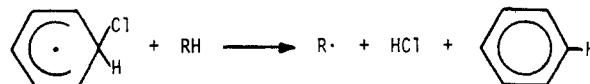


between these species has been fuzzy. Historically, reactions whose products involve substitution or addition on the aromatic nucleus (i.e., reaction at carbon) have generally been interpreted as involving CCH,<sup>1,2</sup> whereas selective hydrogen abstractions from alkanes were attributed to  $\pi\text{C}$ .<sup>1,3</sup>

The original reasons for attributing selective hydrogen abstractions to  $\pi\text{C}$  are no longer valid (vide infra). Furthermore, the notion of a solvent effect on the reactivity of an uncharged radical has depended almost entirely on acceptance of the assignment of  $\pi\text{C}$  structure for  $\text{Cl}^\bullet$  in benzene.<sup>3</sup> It is disconcerting that there is no indication that solvation plays a role in determining the properties of other neutral radicals. Thus, despite the universal acceptance of the concept for 30 years, it is necessary to reconsider the evidence for the  $\pi$ -complex assignment.

Formation of CCH is both reasonable and consistent with available data in the literature. Since 6-halocyclohexadienyl radicals are reported to have appreciable spin density at halogen,

it is also reasonable to consider the possibility that the 6-chlorocyclohexadienyl radical has the capacity to react with an alkane to make an alkyl radical, HCl, and benzene.



**B. Historical.** Chlorine does not react with benzene in the dark. The light-catalyzed reaction leading to the hexachlorocyclohexanes is recognized as a free-radical chain reaction, proceeding with the 6-chlorocyclohexadienyl radical (CCH), made by addition of a chlorine atom to benzene.<sup>1,2,4-8</sup> In the 1950s Russell introduced a third species, the  $\pi$ -complex ( $\pi\text{C}$ ), as the postulated intermediate to explain the more selective chlorination of alkanes in the presence of benzene.<sup>9-12</sup>

(1) For a comprehensive review of free-radical chlorination, see: Poutsma, M. L. In *Methods in Free Radical Chemistry*; Huyser, E. S., Ed.; Marcel Dekker: New York, 1969; Vol. 1, p 79.

(2) For a discussion, see: Rodgers, A. S.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* **1967**, *89*, 4578.

(3) For a review of solvent effects in free-radical chemistry, see: Huyser, E. S. In *Advances in Free-Radical Chemistry*; Williams, G. H., Ed.; Logos: London, 1965; Vol. 1, p 79.

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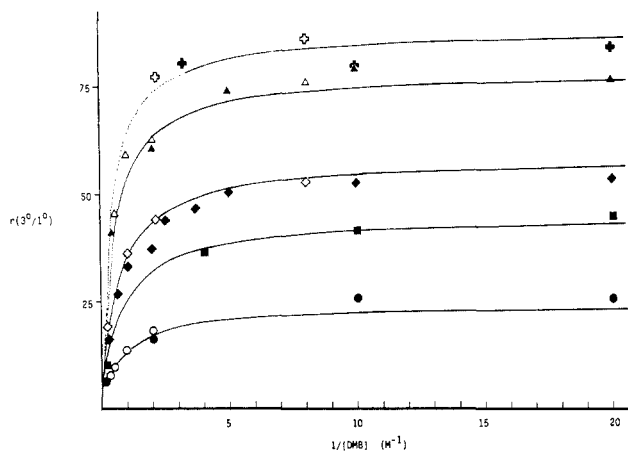
(9) Russell, G. A.; Brown, H. C. *J. Am. Chem. Soc.* **1957**, *79*, 4031.

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(12) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 49.

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**Figure 1.** Photochlorination of 2,3-dimethylbutane (DMB) in benzene; variation of selectivity,  $r(3^\circ/1^\circ)$ , with  $1/[\text{DMB}]$ . Key: 1.0 M PhH, ●; 2.5 M PhH, ■; 4.0 M PhH, ◆; 7.8 M PhH, ▲; 11 M PhH, +. Data appear in Table I. Unshaded figures represent results of Ingold et al., ref 15. Solid lines were computer-generated by using the parameters determined by the NLIN procedure.

Russell's explanation of the selective chlorination of alkanes in arene solvents was based on the hypothesis of an *equilibrium mixture* of a high-selectivity and a low-selectivity intermediate, HSI and LSI, respectively. The hydrogen abstractors were believed to be at equilibrium because the selectivity was invariant with  $[\text{RH}]$ .<sup>10-12</sup>

Russell proposed a chlorine atom/benzene  $\pi$ -complex ( $\pi\text{C}$ ) for the HSI and a free chlorine atom for the LSI;  $\pi\text{C}$  was postulated to be less reactive and for that reason more selective. This explanation enjoyed universal acceptance for 3 decades, although the original base, noncorrelation with phenyl radical selectivities for additions to arenes, had been significantly eroded by the report of nitrophenyl selectivities<sup>13</sup> which correlated nicely with Russell's "solvation effects".

In a preliminary communication<sup>14</sup> (1983) we reported a hitherto unnoticed feature of the chlorination of alkanes in benzene: the selectivity increased with decreasing alkane concentration, reaching a plateau at alkane concentrations below 0.1 M, indicating the Russell experiments did not employ equilibrium mixtures of HSI and LSI. We proposed at that time that (1) only at low alkane concentrations ( $\leq 0.1$  M) were the LSI and HSI at equilibrium and (2) that the reduced rate of formation of HSI, implied by these observations, made the 6-chlorocyclohexadienyl radical (CCH) a more likely candidate for the HSI.

In a recent report, Ingold and co-workers confirmed our experimental findings but argued, largely on the basis of an ambiguous spectroscopic assignment (*vide infra*), for  $\pi\text{C}$  as the HSI.<sup>15</sup> Further, they state that the 6-chlorocyclohexadienyl radical is not an intermediate in the benzene/ $\text{Cl}^\bullet$  system. Currently, this spectroscopic argument is the *only* basis for the  $\pi\text{C}$  assignment.

In this paper, we provide additional details related to our communication and new evidence which defines the connection between high-selectivity hydrogen abstractions and other competitive processes. There is strong support for our earlier proposal that the 6-chlorocyclohexadienyl radical is the main species operating in the benzene/ $\text{Cl}^\bullet$  system. Further, this study illustrates the difficulties encountered in extracting information from a system equilibrating at rates which compete with bimolecular reactions having rates near the diffusion-controlled limit.

## II. Results

### A. Photochlorination of Alkanes in Benzene: LSI/HSI Equilibrium.

Photochlorinations of substrates were carried out

(13) Itô, R.; Migita, T.; Morikawa, N.; Simamura, O. *Tetrahedron* **1965**, *21*, 955.

(14) Skell, P. S.; Baxter, H. N., III; Taylor, C. K. *J. Am. Chem. Soc.* **1983**, *105*, 120.

(15) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Luszyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5464.

**Table I.** Photochlorination of 2,3-Dimethylbutane (DMB) in Benzene at 20 °C ( $\text{CCl}_3\text{F}$  as Diluent)<sup>a</sup>

$[\text{PhH}]^b$	$[\text{DMB}]^b$	$r(3^\circ/1^\circ)_{\text{obsd}}^c$	$r(3^\circ/1^\circ)_{\text{calcd}}^d$
0.25	0.10	13.0	9.1
0.50	0.10	17.6	14
1.0	7.0	6.6	6.3
1.0	0.50	16.1	17
1.0	0.10	25.7	22
1.0	0.05	25.9	23
2.5	6.0	10.1	10
2.5	0.25	36.4	37
2.5	0.10	41.4	41
2.5	0.050	44.8	43
4.0	4.7	16.1	16
4.0	1.7	26.6	28
4.0	1.0	33.2	35
4.0	0.51	37.5	43
4.0	0.40	43.7	46
4.0	0.27	46.6	49
4.0	0.20	50.2	51
4.0	0.10	55.1	54
4.0	0.050	53.5	56
5.0	0.50	46.6	50
6.0	0.10	65.4	66
7.8	2.3	40.9	38
7.8	0.50	60.6	63
7.8	0.20	73.8	71
7.8	0.10	79.2	74
7.8	0.050	76.8	76
11	0.31	80.4	78
11	0.10	84.0	84
11	0.050	84.0	86

<sup>a</sup>  $\text{C}_6\text{H}_{13}\text{Cl}$  yields  $\geq 85\%$  initial  $[\text{Cl}_2] \leq 0.10[\text{DMB}]$ . <sup>b</sup> Molar concentration. <sup>c</sup>  $r(3^\circ/1^\circ) = 6(\text{yield } 3^\circ \text{ RCl}/\text{yield } 1^\circ \text{ RCl})$ . <sup>d</sup> Calculated by using eq 12.

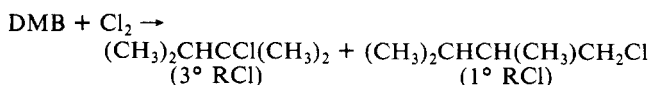
**Table II.** Photochlorination of Pentane in 4.0 M Benzene at 20 °C ( $\text{CCl}_3\text{F}$  as Diluent)<sup>a</sup>

$[n\text{-C}_5\text{H}_{12}]^b$	initial $[\text{Cl}_2]^b$	$r_2(2^\circ/1^\circ)^c$	$r_3(2^\circ/1^\circ)^d$
4.0	0.048	4.9	6.0
1.0	0.049	6.8	8.8
0.20	0.010	8.2	10.7
0.10	0.010	9.7	12.9
0.050	0.0050	9.5	12.6

<sup>a</sup>  $\text{C}_5\text{H}_{11}\text{Cl}$  yields  $\geq 90\%$  with  $\text{C}_5\text{H}_{10}\text{Cl}_2$ 's  $\leq 1\%$ . <sup>b</sup> Molar concentration. <sup>c</sup>  $r_2(2^\circ/1^\circ) = 1.5(\text{yield } 2\text{-chloropentane}/\text{yield } 1\text{-chloropentane})$ . <sup>d</sup>  $r_3(2^\circ/1^\circ) = 3(\text{yield } 3\text{-chloropentane}/\text{yield } 1\text{-chloropentane})$ .

to conversions less than 10% to avoid distortion of the results by further reactions of the products. In most instances this was accomplished by starting with a large ratio of RH to  $\text{Cl}_2$  and otherwise by stopping the reactions at partial conversions. Reactions carried out in the presence of benzene with the ratio  $\text{C}_6\text{H}_6/\text{RH} \leq 120$  gave excellent yields of RCl,  $\sim 95\%$  based on  $\text{Cl}_2$ , but only at low  $\text{Cl}_2$  concentrations.

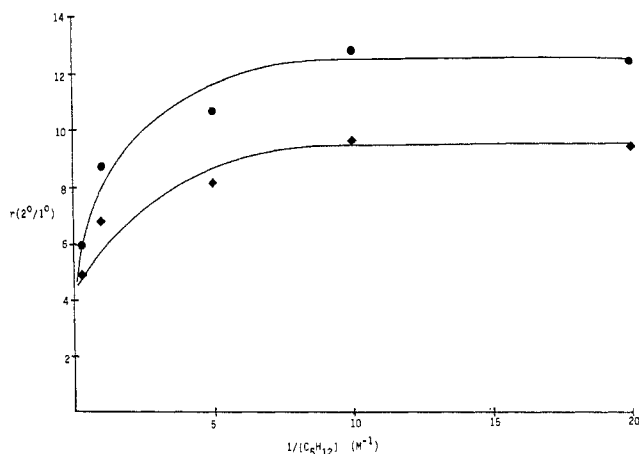
Altering the concentration of substrate 2,3-dimethylbutane (DMB) while maintaining the benzene concentration constant was accomplished with an inert diluent,  $\text{CClF}_3$  or  $\text{CFCl}_2\text{CF}_2\text{Cl}$ . The results appear in Table I and are plotted in Figure 1. The selectivity,  $r(3^\circ/1^\circ)$ , comes close to its maximum value as the



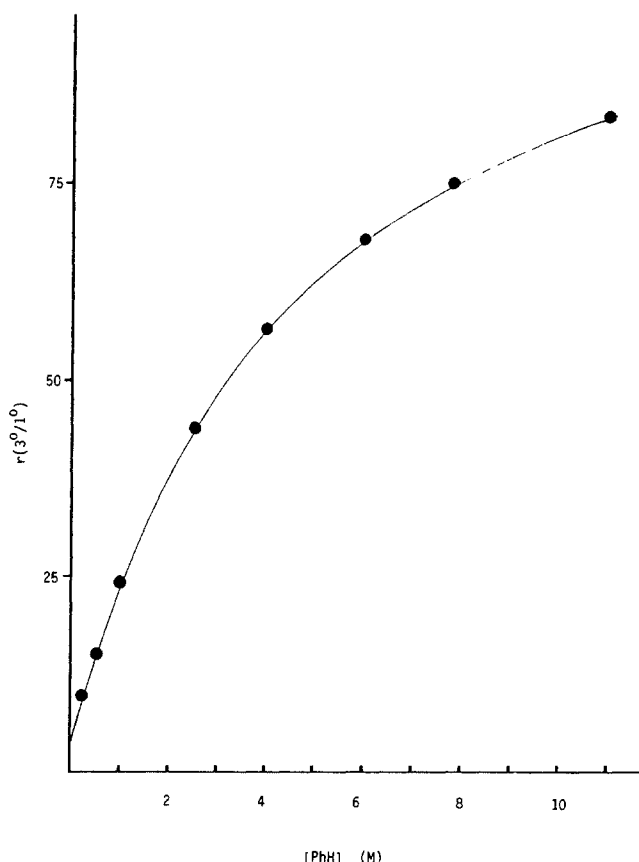
$$r(3^\circ/1^\circ) = 6[3^\circ \text{ RCl}]/[1^\circ \text{ RCl}]$$

concentration of the alkane falls below 0.1 M and remains constant with further decrease of  $[\text{RH}]$ . These plateaus in the plots of  $r$  vs.  $[\text{RH}]^{-1}$  are reached at all benzene concentrations examined. In undiluted benzene and  $< 0.1$  M DMB, selectivities near 90 are observed.

Similar behavior is exhibited in chlorinations of pentane in benzene. At constant benzene concentrations, the selectivities



**Figure 2.** Photochlorination of pentane in 4.0 M benzene; variation of selectivity,  $r(2^\circ/1^\circ)$ , with  $1/[C_5H_{12}]$ . Key:  $r_2(2^\circ/1^\circ)$ ,  $\blacklozenge$ ;  $r_3(2^\circ/1^\circ)$ ,  $\bullet$ . See text and Table II.



**Figure 3.** Photochlorination of 2,3-dimethylbutane (DMB) in benzene; variation of selectivity,  $r(3^\circ/1^\circ)$ , with  $[PhH]$  when  $[DMB] \leq 0.10$  M (plateau region). Data appear in Table I. Solid line was computer-generated by using parameters determined by the NLIN procedure.

increase with decreasing alkane concentration, reaching a plateau value at concentrations of  $\leq 0.1$  M RH (see Table II and Figure 2).

At the plateaus ( $[DMB] \leq 0.1$  M), the selectivities are independent of  $[RH]$  but increase with increasing benzene concentration (Figure 3). Clearly, this is not indicative of 100% conversion of the LSI to the HSI. If such were the case, plateau selectivities would all approach a single value, independent of benzene concentration. The observed variation of plateau selectivity with benzene concentration indicates that the HSI is at equilibrium with the LSI, with concentrations of each large enough to have an effect in determining the selectivity.

Decreasing the RH concentration directly results in a reduction in its rate of reaction with the hydrogen abstractors, giving the

**Table III.** Relative Rates of Photochlorination of 2,4-Dimethylpentane/2,4-Dimethylpentane- $d_{16}$  at 20 °C

solvent	hydrogen	$C_7H_{15}Cl$	$C_7D_{15}Cl$	$k_H/k_D$
	or deuterium exchanged			
none <sup>a</sup>	1°	26.8	14.4	1.86
	2°	16.8	14.6	1.15
	3°	15.3	13.2	1.16
$C_6H_6$ <sup>b</sup>	1°	6.65	3.03	2.19
	2°	23.4	12.6	1.86
	3°	35.3	20.2	1.75

<sup>a</sup> 5.0 mmol of 2,4-dimethylpentane and 5.0 mmol of 2,4-dimethylpentane- $d_{16}$ .  $[Cl_2] \leq 0.1[RH]$ . <sup>b</sup> 0.050 M 2,4-dimethylpentane and 0.050 M 2,4-dimethylpentane- $d_{16}$ .

**Table IV.** Relative Rates of Photochlorination of Cyclohexane/Cyclohexane- $d_{12}$  at 20 °C

solvent	$C_6H_{11}Cl$	$C_6D_{11}Cl$	$k_H/k_D$
	yield, $\mu\text{mol}$	yield, $\mu\text{mol}$	
none <sup>a</sup>	254	216	1.18
$C_6H_6$ <sup>b</sup>	125	67.8	1.84
	69.5	35.9	1.93

<sup>a</sup> 5.0 mmol of cyclohexane and 5.0 mmol of cyclohexane- $d_{12}$ .  $[Cl_2] \leq 0.1[RH]$ . <sup>b</sup> 0.050 M cyclohexane and 0.050 M cyclohexane- $d_{12}$ .

LSI and HSI a longer lifetime for attainment of equilibrium. Thus, the plots of selectivity vs.  $[RH]^{-1}$  are equivalent to plots of the  $[HSI]/[LSI]$  ratio as a function of time. Figures 1 and 2 indicate an asymptotic approach to a sensibly constant selectivity with increasing time, which we attributed to an asymptotic approach to a constant value of  $[LSI]/[HSI]$ . Constancy of the latter composition with increasing time is a criterion for equilibrium. For this reason we suggested the  $[LSI]/[HSI]$  values are equilibrium values when the alkane concentrations are equal to or less than 0.1 M.

At higher-than-plateau concentrations, ( $[DMB] > 0.1$  M), the steady-state value of  $[LSI]/[HSI]$  is larger than the equilibrium value, accounting for the lower selectivities. There are no conditions we have encountered under which these ratios are less than the equilibrium values. This circumstance indicates an important feature of the equilibrium system ( $LSI \rightleftharpoons HSI$ ): it is fed mainly from the left. Since these are chain reactions, it becomes apparent that the LSI is produced in the reaction of alkyl radicals with  $Cl_2$ :  $R^\bullet + Cl_2 \rightarrow RCl + LSI$ . Under no circumstances is the HSI generated as a primary product: it is made from the LSI.

**B. Deuterium Isotope Effects on the Substitution Reaction.** High-resolution gas chromatography makes possible the direct determination of isotope effects since both the protonated and perdeuterated reactants or products are readily separated.

In two sets of experiments, competitive chlorinations were examined with the 1:1 isotopic mixtures of (a) 2,4-dimethylpentane<sup>16</sup> and (b) cyclohexane. The primary isotope effect on the hydrogen abstraction step for both free  $Cl^\bullet$  and for the LSI/HSI equilibrium mixture in benzene solvent was determined. The isotope effects at the primary, secondary, and tertiary positions are given in Tables III and IV.

For *free chlorine atoms* the isotope effects at the 2° and 3° positions of 1.15 are remarkably low; at the 1° position, with a stronger C-H bond, 1.86 is not unexpected. These results are consistent with the low activation energy, near encounter-controlled rates of reaction generally accepted for hydrogen abstractions from alkanes by free chlorine atoms.<sup>1</sup>

In the aromatic solvents the isotope effects at the 2° and 3° positions show the largest change from the free  $Cl^\bullet$  values; the change of isotope effect at the 1° position is small in going from alkanic to aromatic solvents. These results indicate that at the 1° positions, reaction occurs mainly with the LSI present in the

(16) We thank Prof. T. Gaüzman, Institute of Physical Chemistry, Federal School of Technology, Lousanne, Switzerland, for graciously providing us with the sample of 2,4-dimethylpentane- $d_{16}$  used in these experiments.

**Table V.** Photochlorination of 0.10 M 2,3-Dimethylbutane (DMB) in 4.0 M Benzene with Pentane or Neopentane at 20 °C

[C <sub>5</sub> H <sub>12</sub> ], M	pentane		neopentane	
	<i>r</i> (3°/1°) <sup>a</sup>	% C <sub>6</sub> H <sub>13</sub> Cl <sup>b</sup>	<i>r</i> (3°/1°) <sup>a</sup>	% C <sub>6</sub> H <sub>13</sub> Cl <sup>b</sup>
0	55	100	55	100
1.0	37	14	62	41
2.0	31	7.1	58	24
5.2	20	2.6		

<sup>a</sup> *r*(3°/1°) = 6(yield 2-chloro-2,3-dimethylbutane/yield 1-chloro-2,3-dimethylbutane). <sup>b</sup> Yield based upon initial Cl<sub>2</sub>. Unaccounted Cl<sub>2</sub> formed C<sub>5</sub>H<sub>11</sub>Cl's—no dichlorides were observed.

equilibrium mixture. At the 2° and 3° positions, reaction occurs largely with the HSI.

Methylene chloride is less reactive than alkanes in chlorinations with Cl<sub>2</sub>, a methylene chloride hydrogen reacting with free Cl• approximately 0.02× the rate of a 1° hydrogen. Consequently, LSI/HSI equilibrium should be attained with higher concentrations of this reactant than with alkanes. There is no difference in isotope effect for chlorinations in nonaromatic or aromatic solvents, *k<sub>H</sub>*/*k<sub>D</sub>* = 2.8 and 2.9, respectively. It follows that reaction takes place mainly with the LSI and that reaction with the HSI is negligible, even though the HSI is the major component of the equilibrium mixture.

**C. Effect of Added Reagents on the LSI/HSI Equilibrium. Experimental Test for Reaction with the HSI.** At any specific benzene and DMB concentration, a unique value of selectivity is observed, indicative of a unique value of [LSI]/[HSI]. If the observed selectivity of a DMB chlorination were altered by inclusion of another substrate, then it would be evident that this substrate had altered the [LSI]/[HSI] value.

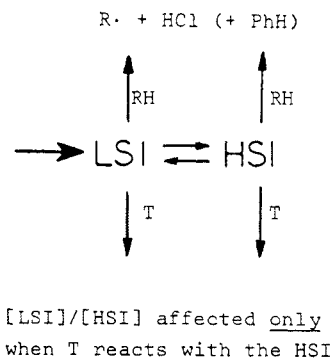
In Scheme I, suppose an added reagent (T) can react with either the LSI or HSI. If an added substrate (T) reacts only with the LSI, what effect should this have on DMB chlorination selectivity? None whatsoever, since the LSI/HSI equilibrating system is fed from the LSI side. Competitive trapping of the LSI by T decreases the concentration of the LSI, but the [LSI]/[HSI] ratio, and hence the observed selectivity, should be unaffected. In contrast, reaction of the HSI with T should decrease the selectivity for DMB chlorination because the [LSI]/[HSI] ratio would be perturbed to a higher than equilibrium value by consumption of the HSI (see Appendix I).

Thus, the effect of an added reagent on the DMB chlorination selectivity could provide a test of whether or not a substrate reacts with the HSI. From the study of a range of substrates and their effect on DMB chlorination selectivity, information regarding the chemistry and the structure of the HSI can be extracted.

**1. Effect of Added Hydrocarbon: Pentane or Neopentane.** The inclusion of pentane, a substance known to react with the HSI,<sup>12</sup> in a "plateau" reaction mixture of 0.1 M DMB in 4.0 M benzene decreases the value of the DMB selectivities (Table V).

In contrast, the inclusion of neopentane in the same mixture has no effect on the DMB selectivity (Table V), indicating the neopentane/HSI reaction does not contribute appreciably to consumption of the HSI, even when formation of neopentyl chloride is the dominant reaction. This conclusion is consistent with that of the isotope effect experiments. It follows that (*k<sub>HSI</sub>*/*k<sub>LSI</sub>*)<sub>neo-C<sub>5</sub>H<sub>12</sub></sub> ≪ (*k<sub>HSI</sub>*/*k<sub>LSI</sub>*)<sub>DMB</sub>.

The neopentane experiment confirms (1) the assertion that reaction of T with the LSI does not alter the [LSI]/[HSI] ratio and (2) that the LSI/HSI system is fed mainly through the LSI

**Scheme I**

side. Furthermore, a subtle feature of the neopentane/DMB results is that they allow an upper limit to be placed on the absolute rate constant for conversion of the LSI to the HSI. Since the yield ratio neopentyl chloride/C<sub>6</sub>H<sub>13</sub>Cl's increases with increasing [Me<sub>4</sub>C], primarily through reaction of Me<sub>4</sub>C with the LSI, it is clear that this reaction is competitive with LSI → HSI. A detailed analysis of the data reveals *k*(Me<sub>4</sub>C + LSI)/*k*(LSI → HSI) ≈ 1.5 M<sup>-1</sup>. Since the bimolecular reaction of neopentane with the LSI cannot exceed the diffusion-controlled limit (≤ 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>), the absolute rate constant for LSI → HSI must be ≤ 7 × 10<sup>9</sup> s<sup>-1</sup>.

**2. Effect of Added *trans*-1,2-Dichloroethene.** The presence of *trans*-1,2-dichloroethene (*trans*-DCE) in a chlorination reaction of 0.1 M DMB in benzene has the same effect as pentane (Table VI). The DMB selectivity is reduced with increasing concentrations of *trans*-DCE. The only product is 1,1,2-tetrachloroethane, indicating the HSI reacts with *trans*-DCE to make the 1,2,2-trichloroethyl radical: HSI + *trans*-CHCl=CHCl → C<sub>6</sub>H<sub>6</sub> + CHCl<sub>2</sub>-C•HCl.

**3. Effect of Added Trichloroethene and Tetrachloroethene.** The presence of trichloroethene in a chlorination reaction of 0.1 M DMB in benzene has the effect of lowering DMB selectivity (Table VII), indicating that Cl<sub>2</sub>C=CHCl reacts with the HSI. Since pentachloroethane is the only product formed, it is apparent that the HSI reacts with Cl<sub>2</sub>C=CHCl in the same manner as with *trans*-DCE, via addition of chlorine atom.

In contrast, tetrachloroethene has no effect on DMB selectivity (Table VII). Thus, Cl<sub>2</sub>C=CCl<sub>2</sub> does not react with the HSI. However, the yield of RCl's decreases steadily with increasing [Cl<sub>2</sub>C=CCl<sub>2</sub>]. As is the case with neopentane, this experiment again demonstrates that substances that consume the LSI have no effect on DMB selectivity.

**4. Effect of High Chlorine Concentration.** The dependence of DMB chlorination selectivity on chlorine concentration in the plateau region, with low conversions of DMB, is shown in Table VIII: with an increase of [Cl<sub>2</sub>] there is a decrease in selectivity. The effect of varying [Cl<sub>2</sub>] in photochlorinations of propane is similar. Propane (0.1 M) in benzene shows, with 0.01 M Cl<sub>2</sub>, *r*(2°/1°) = 9.8; with 1.0 M Cl<sub>2</sub>, *r*'s are 5.6, 6.1, and 6.3 at conversions of propane of 6.2%, 6.9%, and 1.5%, respectively.

The effect of HCl on the relative rates was examined to ascertain the importance of HCl reversal. The inclusions in the reaction mixtures of 5× the anticipated amount of product HCl, or of anhydrous K<sub>2</sub>CO<sub>3</sub> to trap the HCl, had no effect on the selectivity.

The reduction in selectivities indicates that Cl<sub>2</sub> reacts with the HSI. A reasonable expectation is that reaction of HSI with Cl<sub>2</sub>

**Table VI.** Photochlorination of 0.10 M 2,3-Dimethylbutane in the Presence of *trans*-1,2-Dichloroethene (*trans*-DCE) at 20 °C

[ <i>trans</i> -DCE], M	[PhH], M	<i>r</i> (3°/1°) <sub>obsd</sub> <sup>b</sup>	<i>r</i> (3°/1°) <sub>calcd</sub> <sup>c</sup>	C <sub>6</sub> H <sub>13</sub> Cl yield, %	CHCl <sub>2</sub> CHCl <sub>2</sub> yield, %	<i>k<sub>trans-DCE</sub></i> <sup>d</sup> / <i>k<sub>DMB</sub></i>
0	11.2	84	84.5	95		
0.20	11.1	70	84.3	25	80	1.6
1.0	10.3	36	82.2	6.7	94	1.4
1.0	0	3.3	3.96	54.6 <sup>d</sup>	30.2	

<sup>a</sup> [Cl<sub>2</sub>] ≤ 0.10([DMB] + [*trans*-DCE]). <sup>b</sup> *r*(3°/1°) = 6(yield 3° RCl/yield 1° RCl). <sup>c</sup> Selectivity in absence of *trans*-DCE, calculated by using eq 12. <sup>d</sup> 7.1% C<sub>6</sub>H<sub>12</sub>Cl<sub>2</sub>'s; see ref 27.

**Table VII.** Photochlorination of 0.10 M 2,3-Dimethylbutane in 4.0 M Benzene in the Presence of  $\text{Cl}_2\text{C}=\text{CClX}$  ( $\text{X} = \text{Cl}$  or  $\text{H}$ ) at 20 °C

$[\text{Cl}_2\text{C}=\text{CClX}]$ , M <sup>b</sup>	$r(3^\circ/1^\circ)^a$		% $\text{C}_6\text{H}_{13}\text{Cl}$ , % $\text{Cl}_3\text{CCl}_2\text{X}$	
	X = H	X = Cl	X = H	X = Cl
0	55	55	100, 0	100, 0
1	22	55	10, 90	65, 30
2	15	60	5.4, 91	46, 35
5		52		27, 64

<sup>a</sup> $r(3^\circ/1^\circ) = 6(\text{yield } 3^\circ \text{ RCl}/\text{yield } 1^\circ \text{ RCl})$ . <sup>b</sup> $[\text{Cl}_2] \leq 0.01 \text{ M}$ .  $\text{CF}_2\text{ClCCl}_2\text{F}$  used as diluent.

**Table VIII.** Photochlorination of 0.10 M 2,3-Dimethylbutane in Benzene at 20 °C at Varying  $[\text{Cl}_2]$ 

initial $[\text{Cl}_2]$ , M	$r(3^\circ/1^\circ)_{\text{obsd}}^{a,b}$	% yield RCl <sup>c</sup>
0.010	84	95 <sup>d</sup>
1.0	68	27 <sup>e</sup>
2.5	47	30 <sup>e</sup>

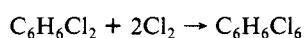
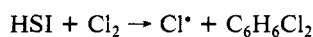
<sup>a</sup> $r(3^\circ/1^\circ) = 6(\text{yield } 2\text{-chloro-2,3-dimethylbutane}/\text{yield } 1\text{-chloro-2,3-dimethylbutane})$ . <sup>b</sup>The benzene molarities in these three experiments and the  $r$  values calculated (eq 12) for very low  $\text{Cl}_2$  concentration are, respectively, 11.2, 84.5; 10.7, 83.3; and 9.9, 81.1. <sup>c</sup> $\text{C}_6\text{H}_{12}\text{Cl}_2$ 's yields are  $\leq 2\%$ . <sup>d</sup>Based on  $\text{Cl}_2$ . <sup>e</sup>Quenched with corn oil; based on RH.

**Table IX.** Photochlorination of 0.050 M Neopentane (500  $\mu\text{mol}$ ) in Benzene (10 mL) at 20 °C

initial $[\text{Cl}_2]$ , M	remaining neopentane, $\mu\text{mol}$	NC <sup>a</sup>	HCH <sup>b</sup>	HCH/NC
0.040	254	246	53	0.22
0.095	226	274	222	0.81
0.22	239	261	337	1.29
0.27	81	419	715	1.71

<sup>a</sup>Neopentyl chloride (calcd),  $\mu\text{mol}$ . <sup>b</sup>1,2,3,4,5,6-Hexachlorocyclohexane,  $\mu\text{mol}$ .

leads to dichlorocyclohexadienes, which are further chlorinated to make hexachlorocyclohexanes.<sup>1,2,4-8</sup>



A predicted consequence is that with an increase of  $[\text{Cl}_2]$ , the ratio of  $\text{C}_6\text{H}_6\text{Cl}_6$  to substitution product (from an alkane substrate) should increase.

This prediction was tested with the photochlorination of neopentane in benzene. The variation of the yield ratio of neopentyl chloride/hexachlorocyclohexanes was observed at different  $\text{Cl}_2$  concentrations, keeping the ratio of neopentane to benzene constant and the neopentane concentration 0.05 M. The qualitative prediction of increase in the addition/substitution ratio with an increase of  $[\text{Cl}_2]$  is confirmed (Table IX).

Consequently, the reductions in selectivities can be attributed to the reaction of  $\text{Cl}_2$  with the HSI by transfer of a chlorine atom to make the dichlorocyclohexadiene.<sup>17</sup>

**5. Effect of Added Maleic Anhydride.** The effect of including maleic anhydride (MA) in the plateau systems for chlorination of DMB is described in Table X. With an increase of MA concentration, the yield of the  $\text{C}_6\text{H}_{13}\text{Cl}$ 's is reduced with a concomitant reduction in selectivity, the selectivity observed at high  $[\text{MA}]$  approaching that characteristic of the LSI. An analogous effect is observed when propane is the substrate (Table XI).

(17) We examined the possibility that little known  $\text{Cl}_3^\cdot$ <sup>18</sup> plays an important role at high chlorine concentrations. (Theoretical treatments indicate small binding energies for this species.<sup>19</sup>) With 1.2 M  $\text{Cl}_2$  in the absence of benzene, photochlorination of a DMB (2.6 M)-neopentane (5.1 M) mixture showed  $r(3^\circ/1^\circ) = 4.1$ , a result identical with that found with  $[\text{Cl}_2] < 0.1 \text{ M}$ .<sup>1,3,10,14,15</sup> If  $\text{Cl}_3^\cdot$  is present in significant amounts, either it does not abstract H-atoms or it does so with the same selectivity as chlorine atom.

(18) Nelson, L. Y.; Pimentel, G. C. *J. Chem. Phys.* **1967**, *47*, 3671.

(19) Ungemach, S. R. *Energy Res. Abstr.* **1978**, *3*(9), Abstract 21947.

**Table X.** Photochlorination of 0.10 M 2,3-Dimethylbutane<sup>a</sup> in Benzene with Maleic Anhydride (MA) at 20 °C

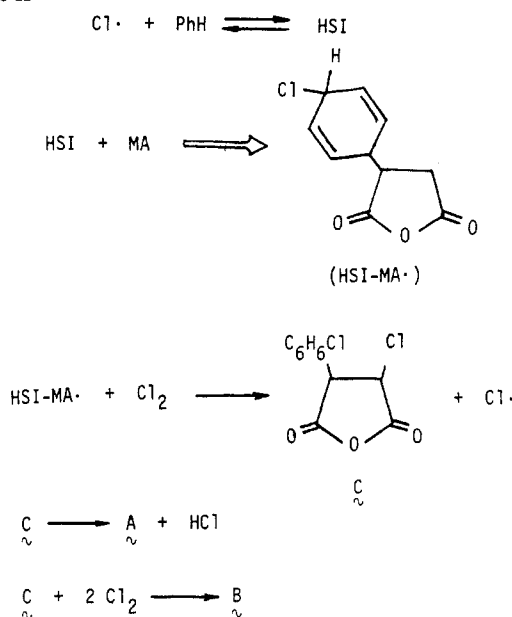
$[\text{MA}]$ , M	$r(3^\circ/1^\circ)^{b,c}$	% yield based on $\text{Cl}_2$
0	84	86
0.10	69	67
0.48	48	43
1.7	29	14
4.1	9.2	

<sup>a</sup> $[\text{Cl}_2] \leq 0.1[\text{DMB}]$ . <sup>b</sup> $r(3^\circ/1^\circ) = 6(\text{yield } 2\text{-chloro-2,3-dimethylbutane}/\text{yield } 1\text{-chloro-2,3-dimethylbutane})$ . <sup>c</sup>The benzene molarities in these experiments and the  $r$  values (eq 12) for very low  $\text{Cl}_2$  concentrations are, respectively, 11.2, 84.5; 11.1, 84.3; 10.8, 83.5; 9.7, 80.6; and 7.8, 74.3.

**Table XI.** Photochlorination of 0.10 M Propane in Benzene with Maleic Anhydride at 70 °C

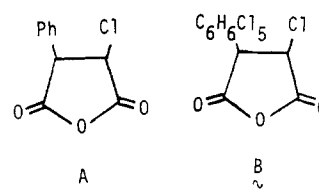
$[\text{MA}]$ , M	initial $[\text{Cl}_2]$ , M	$r(2^\circ/1^\circ)^a$	% yield RCl based on $\text{Cl}_2$	% yield DSA based on $\text{Cl}_2^b$
0	0.010	9.8	97	
0.8	0.010	5.4	7.9	<2
1.7	0.031	4.5 <sup>c</sup>	6.6	7.7
4.1	0.096	3.8 <sup>c</sup>		9.7

<sup>a</sup> $r(2^\circ/1^\circ) = 3(\text{yield } 2\text{-chloropropane}/\text{yield } 1\text{-chloropropane})$ . <sup>b</sup> Dichlorosuccinic anhydride. <sup>c</sup>Same value obtained in another experiment in which special care was taken to minimize gas volume and protect the gas phase from light with aluminum foil.

**Scheme II**

Clearly, maleic anhydride is a substrate which reacts with the HSI.

The nature of the reaction of the HSI with MA comes from the work of Ecke et al.<sup>20</sup> Maleic anhydride intercepts an intermediate in the photochlorination of benzene, yielding two major products, A and B. In work which will be described elsewhere, we confirm their findings.



The only reasonable mechanism for the formation of these products involves trapping of the HSI by reaction at carbon.<sup>21</sup>

(20) Ecke, G. C.; Buzbee, L. R.; Kolka, A. J. *J. Am. Chem. Soc.* **1956**, *78*, 79.

This notion is summarized in Scheme II.

Unlike *trans*-DCE or  $\text{Cl}_2\text{C}=\text{CHCl}$ , which react with the HSI only by transfer of  $\text{Cl}^\bullet$ , MA reacts by addition to the aromatic nucleus.

**D. Effect of  $\text{O}_2$  on the Photochlorination of Benzene.** A major part of the rationale<sup>15</sup> for ascribing the observed UV-vis spectrum of  $\text{Cl}^\bullet$  in benzene to  $\pi\text{C}$ , in deference to CCH, rests upon the assumption that the rate of the  $\text{CCH}/\text{O}_2$  reaction is similar to that of  $\text{C}_6\text{H}_7^\bullet/\text{O}_2$ , the latter of which occurs with a rate at or near the diffusion-controlled limit. For this reason, we examined the effect of  $\text{O}_2$  on the photochlorination of benzene.

In the presence of  $\text{O}_2$ , two products result from the photochlorination of benzene: chlorobenzene and hexachlorocyclohexane. These products arise from competitive trapping of the 6-chlorocyclohexadienyl radical by  $\text{O}_2$  with loss of the ipso H, yielding chlorobenzene and  $\text{HO}_2^\bullet$ ,<sup>22</sup> and by  $\text{Cl}_2$ , yielding dichlorocyclohexadiene and ultimately  $\text{C}_6\text{H}_6\text{Cl}_6$ .<sup>1,2,4-8</sup> The ratio of these products is predicted by eq 1.

$$\frac{[\text{PhCl}]}{[\text{C}_6\text{H}_6\text{Cl}_6]} = \frac{k_{\text{Cl}_2} [\text{Cl}_2]}{k_{\text{O}_2} [\text{O}_2]} \quad (1)$$

Benzene solutions, maintained at 0.05 M in  $\text{Cl}_2$  with  $\text{O}_2$  concentrations of 0.002 or 0.010 M, upon prolonged irradiation were found to produce 967  $\mu\text{mol}$  of  $\text{C}_6\text{H}_6\text{Cl}_6/6.5 \mu\text{mol}$  of PhCl or 403  $\mu\text{mol}$  of  $\text{C}_6\text{H}_6\text{Cl}_6/12.3 \mu\text{mol}$  of PhCl, respectively. Therefore, the rate constant ratio  $k_{\text{Cl}_2}/k_{\text{O}_2} = 6.3$  (average).

These results indicate that trapping of CCH by  $\text{O}_2$  is slower than reaction with  $\text{Cl}_2$ , implying that for CCH, the rate of the  $\text{O}_2$  reaction is considerably slower than for unsubstituted cyclohexadienyl radical. As is elaborated in the Discussion section, this result, and other considerations, cripples the conclusion<sup>15</sup> that [CCH], if present at all, is  $\ll 1\%$ .

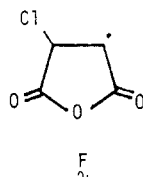
### III. Discussion

**A. Identity of the HSI. 1. Nature of the Species Trapped by Added Reagents.** In the preceding section, it was shown that some reagents react with the HSI at chlorine (secondary and tertiary hydrogens of alkanes, *trans*-DCE, and  $\text{Cl}_2\text{C}=\text{CHCl}$ ), while others react at carbon ( $\text{Cl}_2$  and MA). On the basis of this chemistry, we turn our attention to a discussion of structures for the HSI which would be consistent with the observed chemistry.

The  $\pi$ -complex is well considered as a chlorine atom solvated by benzene, with neither component undergoing any large electronic or structural alteration in making the complex,<sup>23</sup> while CCH has a distinctly different set of covalent bonds, bond angles, and electron distribution.

Chlorine does not react with benzene in the dark or in the absence of electrophilic catalysts. Neither maleic anhydride nor  $\text{O}_2$  reacts with benzene under any conditions. It is reasonable to suppose the reaction of the aromatic portion of the  $\pi$ -complex (i.e.,

(21) There is no precedent for a reverse mechanism for formation of C, namely, addition of F to benzene, followed by trapping with  $\text{Cl}_2$ . Further,



addition of  $\text{Cl}_2$  to maleic anhydride, which involves F as an intermediate, is a slow reaction, both in the dark and when photoinitiated. Formation of the dichlorosuccinic anhydrides in the presence of benzene, as in Table X, is not an important reaction (<2% yield with 0.8 M MA and 9.7% yield with 4.1 M MA). A competitive photochlorination of 1 M MA with 1 M *trans*-1,2-dichloroethene in  $\text{CDCl}_3$  with 481  $\mu\text{mol}$  of  $\text{Cl}_2$  produced 34  $\mu\text{mol}$  of dichlorosuccinic anhydride and 442  $\mu\text{mol}$  of 1,1,2,2-tetrachloroethane, indicating a rate constant ratio for addition of  $\text{Cl}^\bullet$  of 0.08. Thus, MA is a relatively low reactivity substrate toward free  $\text{Cl}^\bullet$ .

(22) (a) Criegee, R. In *Houben-Weyl Methoden der Organischen Chemie*, 4th ed.; Muller, E., Ed.; George Thieme Verlag: Stuttgart, 1953; Vol. 8, p 16. (b) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1967**, *45*, 785. (c) Hendry, D. G.; Schuetzle, D. *J. Am. Chem. Soc.* **1975**, *97*, 7123.

(23) Tamres, M.; Strong, R. L. In *Molecular Association*; Foster, R., Ed.; Academic: New York, 1979; Vol. 2, p 331.

reaction at carbon) with these reagents to be as slow (or slower) since the  $\pi$ -complex is expected to have negligible odd-electron character at carbon.<sup>24</sup> For the type of  $\pi$ -complex Russell proposed, neither at that time nor at the present is there any evidence in the literature for bimolecular reactions at the carbon atoms.

In contrast, the 6-chlorocyclohexadienyl radical, resulting from the introduction of a formal  $\sigma$ -bond, is expected to have appreciable spin density at both the out-of-plane chlorine and hydrogen atoms, as well as at the carbons of the aromatic nucleus. Thus, it is expected that CCH would be distinguished by chemistry at all these positions.

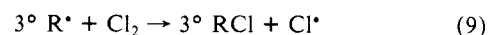
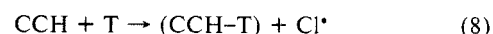
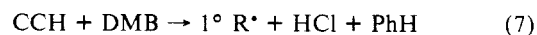
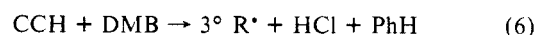
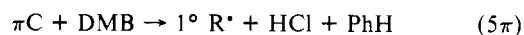
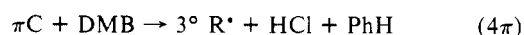
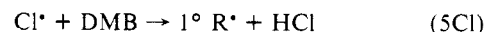
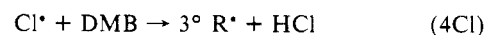
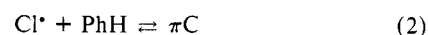
The preceding rationale represents the "classical" chemical approach to this problem. In Russell's pioneering work, one of his original arguments against CCH as the HSI centered on the failure to detect either hexachlorocyclohexanes or chlorobenzene (resulting from trapping of the HSI by  $\text{Cl}_2$  at carbon).<sup>10</sup> But, both of these are products under appropriate conditions.

Thus, we are forced to conclude that the intermediate trapped by  $\text{Cl}_2$ , MA, and  $\text{O}_2$  is the 6-chlorocyclohexadienyl radical.

**2. Is the 6-Chlorocyclohexadienyl Radical the HSI?** The experimental data clearly establish that an intimate link exists between the HSI and the 6-chlorocyclohexadienyl radical: there is an increase in the [LSI]/[HSI] ratio (decrease in selectivity) when reagents are present which react with CCH. Thus, CCH is an important component of the PhH/ $\text{Cl}^\bullet$  system. However, these results do not unambiguously establish that the HSI is the CCH. The alternative is that the CCH is in rapid equilibrium with  $\pi\text{C}$ , which is the HSI.

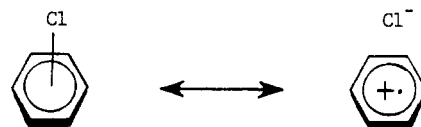
In Scheme III contributions from three potential hydrogen abstractors to the observed selectivity are indicated: free chlorine atom,  $\pi\text{C}$ , and CCH. In this mechanism free chlorine atom is a contributor to LSI behavior, and two possibilities are considered for HSI behavior: (1)  $\pi\text{C}$  is the HSI, in rapid equilibrium with CCH, or (2) CCH is the HSI, and  $\pi\text{C}$  is either kinetically insignificant (as far as H-abstractions are concerned) or a component of the LSI mixture.

#### Scheme III<sup>a</sup>

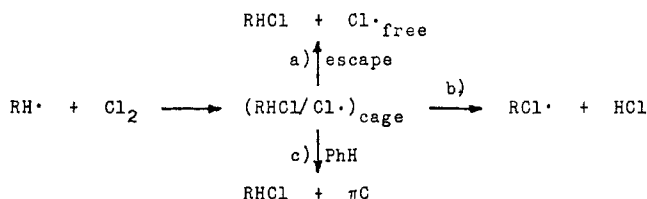


<sup>a</sup>If  $\text{T} = \text{Cl}_2$ , then eq 8 becomes  $\text{CCH} + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_6\text{Cl}_2 + \text{Cl}^\bullet$ . If  $\text{T} = \textit{trans}$ -DCE, then eq 8 becomes  $\text{CCH} + \textit{trans}$ -DCE  $\rightarrow$  PhH +  $\text{Cl}_2\text{CH}-\text{CH}^\bullet\text{Cl}$ . If  $\text{T} = \textit{maleic}$  anhydride (MA), then CCH-T is an addition product.

(24) While it is possible to draw a hybrid  $\pi$ -complex structure with spin density at carbon to describe the ground state, the ionic structure should make small contributions because it is a high-energy species in the absence of any stabilizing interactions (e.g., solvation). Further, neither of these canonical structures would serve to explain the high rate of addition to maleic anhydride, since both of the reactants are electron-deficient species.



## Scheme IV



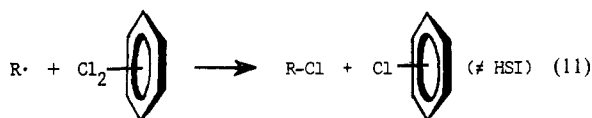
The experimental results thus far reported do not allow the identity of the HSI to be uniquely determined. However, when considered in conjunction with other information, we believe that the CCH emerges as the strongest candidate for the HSI.

**3. Anomalies Which Attend the Assumption That the  $\pi$ -Complex Is the HSI.** Several aspects of the selective substitution of alkanes are difficult to understand if one argues that the HSI is the  $\pi$ -complex.

(a) The observed selectivity of DMB photochlorinations is lowered when reagents which react with CCH are present. In order to rationalize the decrease in selectivity (increase in [LSI]/[HSI]), it would be necessary to conclude that equilibrium between  $\pi\text{C}$  and the CCH must be established *more rapidly* than equilibrium is established between  $\pi\text{C}$  and free chlorine atom.

This conclusion is bizarre when one considers  $\pi\text{C}$  is simply a benzene-solvated chlorine atom which by analogy to  $\text{I}^{\cdot}/\text{PhH}$  behavior should be formed in less than 10 ps in benzene,<sup>25,26</sup> a reasonable time for the reorientation of solvent molecules necessary for solvation. Conversely, CCH is the result of a formal chemical reaction: formation of a  $\sigma$ -bond between carbon and chlorine to form a species with distinctly different bond angles and electron distribution (i.e., disruption of aromaticity in the benzene ring). We find it unreasonable to suppose that  $\pi\text{C}$  would reach equilibrium with CCH faster than with free Cl atom.

(b) Since  $\text{Cl}_2$  is  $\pi$ -complexed to benzene,<sup>33</sup> it is reasonable to suppose that abstraction of Cl from such a complex (eq 11) would produce the chlorine atom  $\pi$ -complex as the primary product. Reaction of  $\text{R}^{\cdot}$  with benzene-solvated  $\text{Cl}_2$  should produce solvated  $\text{Cl}^{\cdot}$ .



However, since reaction of alkyl radical with  $\text{Cl}_2$  produces the LSI, this consideration would exclude the  $\pi$ -complex as the HSI and imply that  $\pi\text{C}$  is the LSI.

**4. Role of the  $\pi$ -Complex in the PhH/ $\text{Cl}^{\cdot}$  System.** It has been shown that low-conversion  $\text{Cl}_2$  chlorinations of low-concentration alkanes in inert solvents ( $\text{CCl}_4$  and  $\text{CFCl}_3$ ) result in extensive multiple substitution, introducing two or three chlorine substituents, rather than one.<sup>27</sup> This observation is the consequence of a cage "phenomenon", illustrated in Scheme IV. Reaction of alkyl radical ( $\text{RH}^{\cdot}$ ) with  $\text{Cl}_2$  initially produces the caged pair ( $\text{RHCl} + \text{Cl}^{\cdot}$ ). Abstraction of a second hydrogen from  $\text{RHCl}$  by  $\text{Cl}^{\cdot}$  (path

b) is closely competitive with cage escape (path a). Some understanding of the nature of the  $\pi$ -complex is derived from the observation that benzene precludes multiple chlorinations. For example, photochlorination of 0.1 M DMB in  $\text{CFCl}_3$  (an inert solvent) yields only 40%  $\text{RCl}^{\cdot}$ s, due to polychloride formation (60%) via the mechanism outlined in Scheme IV. In contrast, the same reaction carried out in the presence of benzene (2.5–11 M) as solvent yields >93% monochlorides, with no detectable polychloride formation.

Polychloride formation is an intrinsic property of  $\text{Cl}^{\cdot}$ , the consequence of producing an extremely reactive species in close proximity to a potential substrate ( $\text{RHCl}$ ). The only explanation for these results is that *when benzene is the solvent, reaction of alkyl radical with  $\text{Cl}_2$  forms an intermediate lower in reactivity than  $\text{Cl}^{\cdot}$* . When it is recalled that the reaction  $\text{R}^{\cdot} + \text{Cl}_2$  produces the LSI, it becomes clear that *the LSI is an intermediate lower in reactivity than  $\text{Cl}^{\cdot}$*  (i.e.,  $\text{Cl}^{\cdot}$  cannot be the LSI). A reasonable conclusion is that this lower reactivity intermediate is the  $\pi$ -complex, leaving as a corollary that the HSI must be the 6-chlorocyclohexadienyl radical.

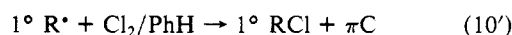
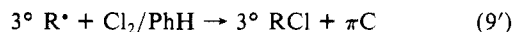
Two propagation steps can be considered for the direct formation of  $\pi\text{C}$  from  $\text{R}^{\cdot} + \text{Cl}_2$ . (1) Alkyl radical reacts with  $\pi$ -complexed  $\text{Cl}_2$  ( $\text{Cl}_2/\text{PhH}$ ), yielding the  $\text{Cl}^{\cdot}/\text{PhH}$   $\pi$ -complex directly (eq 11). (2) When  $\text{RH}^{\cdot}$  reacts with  $\text{Cl}_2$ , generating the  $\text{RHCl}/\text{Cl}^{\cdot}$  caged pair, the presence of benzene provides a third pathway for removal of  $\text{Cl}^{\cdot}$  which is *faster* than both cage escape (path a, Scheme IV) and H-abstraction from  $\text{RHCl}$  (path b). With the realization that the cage is now composed of and surrounded by benzene molecules, rather than an inert solvent, this "third" pathway must involve direct reaction of  $\text{Cl}^{\cdot}$  with  $\text{PhH}$ , and the product of this reaction is most likely  $\pi\text{C}$  (path c).

Mechanism 2 requires that  $\pi\text{C}$  formation be faster than the other competitive pathways, H-abstraction from  $\text{RHCl}$  or cage escape. On the basis of available literature data, this conclusion appears likely. Although the intrinsic rate of formation of  $\pi\text{C}$  is unknown, formation of  $\text{I}^{\cdot}/\text{arene}$   $\pi$ -complexes occurs in  $\ll 10$  ps.<sup>25,26</sup> It is unlikely that formation of  $\pi\text{C}$  would be any slower.

In either instance, the propagation step is characterized by exactly the same overall stoichiometry:  $\text{R}^{\cdot} + \text{Cl}_2/\text{PhH} \rightarrow \text{RCl} + \pi\text{C}$ .

These results *cannot* be explained by a two-intermediate system which would assign LSI behavior to free chlorine atom and HSI behavior to  $\pi\text{C}$ . Such a mechanism would require free  $\text{Cl}^{\cdot}$  to be produced from the reaction of alkyl radicals with  $\text{Cl}_2$  in benzene, and as a consequence, *multiple chlorination should have been observed*.

In order to account for *all* the experimental results and not only DMB selectivity, the mechanism we prefer for the photochlorination of DMB in benzene entails replacing eq 9 and 10 of Scheme III by 9' and 10'.



$\pi$ -complexed  $\text{Cl}_2$  ( $\text{Cl}_2/\text{PhH}$ ) produce  $\pi\text{C}$  directly rather than free Cl atom. LSI behavior is assigned to the  $\text{Cl}^{\cdot}/\pi\text{C}$  equilibrium mixture and HSI behavior to CCH. This mechanism will henceforth be referred to as Scheme III'.

**B. Kinetic Analysis.** Schemes III and III' predict a relationship between the observed selectivity,  $r(3^{\circ}/1^{\circ})$ , and the concentrations of  $\text{PhH}$ , DMB, and T. The supplementary material describes the results obtained when variation of these concentrations is reconciled to the observed DMB selectivity in a quantitative manner.

A kinetic analysis of the dependence of DMB photochlorination selectivity on  $[\text{DMB}]$ ,  $[\text{PhH}]$ , and  $[\text{T}]$ , based upon Scheme III', yields the following relative reactivity order for CCH: maleic anhydride (6) > *trans*-dichloroethylene (5) > 2,3-dimethylbutane (2) > pentane (1) >  $\text{Cl}_2$  [1.00] > neopentane,  $\text{CH}_2\text{Cl}_2$  (<0.1).

Three key absolute rate constants emerge from the Ingold laser flash photolysis study: (1)  $\text{Cl}^{\cdot} + \text{PhH} \rightarrow \text{HSI}$ , (2)  $\text{Cl}^{\cdot} + \text{RH} \rightarrow \text{R}^{\cdot} + \text{HCl}$ , and (3)  $\text{HSI} + \text{RH} \rightarrow \text{R}^{\cdot} + \text{HCl} + \text{PhH}$ .<sup>15</sup> By use of these and the rate constant ratios obtained from our own kinetic

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(26) Hilinski, E. F.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1985**, *107*, 5907.

(27) Skell, P. S.; Baxter, H. N., III. *J. Am. Chem. Soc.* **1985**, *107*, 2823.

(28) The equilibrium constant for  $\pi$ -complex formation between hexamethylbenzene and  $\text{I}^{\cdot}$  is  $2.7 \text{ L mol}^{-1}$ <sup>29</sup> and  $1.7 \text{ L mol}^{-1}$  with  $\text{I}_2$ .<sup>30</sup> Likewise, with *o*-xylene,  $K_{\text{EQ}}$  is  $7.4 \text{ L mol}^{-1}$ <sup>31</sup> and  $2.96 \text{ L mol}^{-1}$ <sup>32</sup> for  $\text{I}^{\cdot}$  and  $\text{I}_2$ , respectively. If analogy applies, the equilibrium constant for  $\text{Cl}_2 + \text{PhH} \rightarrow (\text{Cl}_2 \rightarrow \text{PhH})$  of  $0.33 \text{ L mol}^{-1}$ <sup>33</sup> indicates an equilibrium constant for  $\text{Cl}^{\cdot} + \text{PhH} \rightarrow \pi\text{C}$  to be on the order of  $0.6 \text{ L mol}^{-1}$ . Thus, in pure benzene,  $[\pi\text{C}]/[\text{Cl}^{\cdot}] \sim 6$ .

(29) Strong, R. L.; Perano, J. J. *J. Am. Chem. Soc.* **1961**, *83*, 2843.

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Table XII. Estimates of Absolute Rate Constants for Key Reactions in the PhH/Cl<sup>•</sup> System

reaction		estimate <sup>a</sup> of rate const <sup>b</sup> based upon	
		Scheme III	Scheme III'
(3Cl)	Cl <sup>•</sup> + DMB → 3° R <sup>•</sup> + HCl	1.3 × 10 <sup>9c</sup>	1.3 × 10 <sup>9c</sup>
(4Cl)	Cl <sup>•</sup> + DMB → 1° R <sup>•</sup> + HCl	2.0 × 10 <sup>9c</sup>	2.0 × 10 <sup>9c</sup>
(1)	Cl <sup>•</sup> + PhH → πC		6.0 × 10 <sup>9c,d</sup>
(-1)	πC → Cl <sup>•</sup> + PhH		≤ 6 × 10 <sup>9</sup>
(3π)	πC + DMB → 3° R <sup>•</sup> + HCl + PhH		≤ 6 × 10 <sup>8</sup>
(4π)	πC + DMB → 1° R <sup>•</sup> + HCl + PhH		≤ 3 × 10 <sup>8</sup>
(2)	πC → CCH		≤ 10 <sup>10e</sup>
(-2)	CCH → πC		6 × 10 <sup>7</sup>
(2')	Cl <sup>•</sup> + PhH → CCH	6.0 × 10 <sup>9c</sup>	6 × 10 <sup>9c</sup>
(-2')	CCH → Cl <sup>•</sup> + PhH	3 × 10 <sup>7</sup>	6 × 10 <sup>7</sup>
(5)	CCH + DMB → 3° R <sup>•</sup> + HCl + PhH	4.6 × 10 <sup>7c</sup>	4.6 × 10 <sup>7c</sup>
(6)	CCH + DMB → 1° R <sup>•</sup> + HCl + PhH	2 × 10 <sup>6</sup>	≤ 2 × 10 <sup>6</sup>
(7-Cl <sub>2</sub> )	CCH + Cl <sub>2</sub> → C <sub>6</sub> H <sub>6</sub> Cl <sub>2</sub> + Cl <sup>•</sup>	3 × 10 <sup>7</sup>	2 × 10 <sup>7</sup>
(7-MA)	CCH + MA → CCH-MA <sup>•</sup>	2 × 10 <sup>8</sup>	1 × 10 <sup>8</sup>
(7-trans-DCE)	CCH + trans-DCE → PhH + Cl <sub>2</sub> CHCHCl	2 × 10 <sup>8</sup>	9 × 10 <sup>7</sup>
(7-n-C <sub>5</sub> H <sub>12</sub> )	CCH + n-C <sub>5</sub> H <sub>12</sub> → C <sub>5</sub> H <sub>12</sub> <sup>•</sup> + PhH + HCl	3 × 10 <sup>7</sup>	3 × 10 <sup>7</sup>
(7-O <sub>2</sub> )	CCH + O <sub>2</sub> → PhCl + HO <sub>2</sub> <sup>•</sup>	5 × 10 <sup>6</sup>	5 × 10 <sup>6</sup>

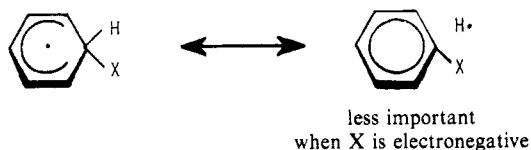
<sup>a</sup> See ref 56 for a discussion of discrepancies between these rate constants and observed substitution yields. <sup>b</sup> Rate constants in units M<sup>-1</sup> s<sup>-1</sup> or s<sup>-1</sup>. <sup>c</sup> Laser flash photolysis results, ref 15. <sup>d</sup> Assumed to be diffusion controlled. <sup>e</sup> Based upon the thesis that LSI → HSI occurs in ~10<sup>-9</sup> s.

analysis, the rate constants for various steps are obtained (collected in Table XII). From these, it is possible to calculate the following equilibrium constants, based upon Scheme III':



Our estimate of the equilibrium constant for π-complex formation (ca. unity) is of the same magnitude as that reported for I<sup>•</sup>/arene π-complexes.<sup>28</sup>

**C. Literature Precedent. UV, IR, and ESR Spectroscopies. Cyclohexadienyl Radicals and π-Complexes.** ESR spectra have not yet been obtainable for the PhH/Cl<sup>•</sup> system, although they have been found for the other halogens. The ESR spectra of 6-fluorocyclohexadienyl radicals, formed by the reaction of F<sup>•</sup> with C<sub>6</sub>H<sub>6</sub> (or C<sub>6</sub>D<sub>6</sub>)<sup>34</sup> or by the reaction of H<sup>•</sup> with C<sub>6</sub>F<sub>6</sub>,<sup>35</sup> are reported. Hyperfine coupling (hfc) to F is on the order of 125–130 G. The hfc to the out-of-plane H-atom is 19.3 G, lower than that of an unsubstituted cyclohexadienyl radical (48 G).<sup>36</sup> This decrease is attributed to a lowering of the energy of the C–H orbital by introduction of an electronegative substituent, thereby decreasing the degree of hyperconjugation<sup>35</sup> (see below). Similar results are reported for the 6-hydroxycyclohexadienyl radical: hyperfine coupling to the ipso H is 36.0 G.<sup>37</sup>



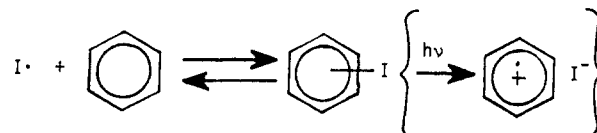
Unlike the case of I<sup>•</sup> or Br<sup>•</sup>, there is no evidence for a π-complex formed by the interaction of F<sup>•</sup> and PhH. Jacox reports that at 14 K, the interaction of F<sup>•</sup> with benzene produces a species whose IR absorption can only be attributed to the 6-fluorocyclohexadienyl radical.<sup>38</sup> No other intermediate was detected.

ESR spectra for the corresponding 6-bromo- and 6-iodo-cyclohexadienyl radicals have been reported by Symons et al.<sup>39,40</sup> These radicals, produced by the ipso protonation of the corre-

sponding halobenzene radical anion, exhibit large hyperfine coupling to I (or Br). The hfc to the out-of-plane hydrogen (35–40 G) is diminished from that of an unsubstituted cyclohexadienyl radical (48 G).<sup>41</sup>

Shida and Hanazaki<sup>43</sup> and Jordan et al.<sup>44</sup> report excellent UV spectra for C<sub>6</sub>H<sub>7</sub><sup>•</sup>, dominated by an absorption at 318 nm, with weak features at 510 and 550 nm. The latter are attributed to charge-transfer interactions between the π-electrons and the out-of-plane C–H bonds.<sup>43</sup> The 6-hydroxycyclohexadienyl radical, formed by the addition of HO<sup>•</sup> to benzene, is characterized by a broad absorption centered at 313 nm.<sup>45</sup>

Interactions of I<sup>•</sup> and Br<sup>•</sup> with benzene involve the formation of charge-transfer complexes<sup>46,47</sup> (see below), characterized by broad UV absorptions at λ<sub>max</sub> = 500 and 560 nm, respectively; the literature contains no report of shorter wavelength absorptions. The formation of the π-complex from free I<sup>•</sup> is complete in arene solvents in <<10 ps,<sup>25,26</sup> indicating a rate constant of >>10<sup>11</sup> s<sup>-1</sup>.



Bühler and co-workers reported a broad visible absorption (200 nm wide) centered at 490 nm in pulse-radiolyzed CCl<sub>4</sub> in benzene which was attributed to a Cl<sup>•</sup>/PhH π-complex and a strong, poorly resolved UV band at ~320 nm.<sup>48,49</sup> The reported equilibrium constant for the formation of this complex from Cl<sup>•</sup> and C<sub>6</sub>H<sub>6</sub> is >10<sup>3</sup> M<sup>-1</sup>, based upon a Benesi–Hildebrand analysis.<sup>49</sup> The decay of the transient followed first-order kinetics with a half-life of (1–10) × 10<sup>-6</sup> s. On the basis of this observation, and by analogy to the Br<sup>•</sup>/PhBr π-complex which decomposes unimolecularly via addition of Br<sup>•</sup> to the arene, with a rate constant of 5.4 (±0.2) × 10<sup>4</sup> s<sup>-1</sup>,<sup>47,50</sup> Bühler argued that the mechanism of

(34) Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Phys. Chem.* **1970**, *74*, 2083.

(35) Yim, M. B.; Wood, D. E. *J. Am. Chem. Soc.* **1975**, *97*, 1004.

(36) Devolder, P.; Goudmand, P. *C. R. Seances Acad. Sci, Ser. A* **1975**, *280*, 1281.

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(38) Jacox, M. E. *J. Phys. Chem.* **1982**, *86*, 670.

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(40) Mishra, S. P.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 185.

(41) These assignments must be viewed with some degree of skepticism. Recent studies of the Birch reduction indicate that ipso protonation of similarly substituted benzene radical anions, under thermodynamic or kinetic control, is unfavorable relative to ortho, meta, or para protonation.<sup>42</sup> However, Symons attributes the observed ESR spectra to *exclusive* ipso protonation and does not observe any other isomeric halocyclohexadienyl radicals.<sup>39,40</sup>

(42) Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 4074.

(43) Shida, T.; Hanazaki, I. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 646.

(44) Jordan, J. E.; Pratt, D. W.; Wood, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 5588.

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(47) For a review, see: Bühler, R. E. *Radiat. Res. Rev.* **1972**, *4*, 233.

(48) Bühler, R. E.; Ebert, M. *Nature (London)* **1967**, *214*, 1220.

(49) Bühler, R. E. *Helv. Chim. Acta.* **1968**, *51*, 1558.

(50) Bühler, R. E.; Bossy, J. M. *Int. J. Radiat. Phys. Chem.* **1974**, *6*, 95.



decay undoubtedly involved the conversion of the  $\pi$ -complex to the 6-chlorocyclohexadienyl radical.<sup>47,49</sup>

Ingold and co-workers<sup>15</sup> studied the spectra and kinetics of transients generated by flash photolysis of a number of  $\text{Cl}^*$  precursors ( $\text{Cl}_2$ ,  $t\text{-BuO}^* + \text{HCl}$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_5\text{COCH}_2\text{Cl}$ , and  $\text{Cl}_2\text{SO}$ ) in dilute benzene and reported the same spectral features. In addition, these workers also reported that the relative intensities of the two bands remained unchanged over the temperature range  $-14$  to  $+57$  °C, suggesting they were due to either (a) a single species or (b) two discrete species for which  $\Delta H$  of interconversion is  $<0.2$  kcal/mol. They accepted Bühler's assignment of the 490-nm band to the  $\pi$ -complex,<sup>48,49</sup> based upon similarity to broad absorptions in  $\text{I}^*/\text{arene}$  (or  $\text{Br}^*/\text{arene}$ ) systems, but went beyond to the conclusion that the 6-chlorocyclohexadienyl radical was either not formed or formed in unimportant amounts ( $<1\%$ ) relative to the  $\pi$ -complex. However, the stronger, short-wavelength ( $<330$  nm) absorption resembles that of a cyclohexadienyl radical, and in the absence of extinction coefficients, estimates of the relative amounts of the two species cannot be made.<sup>53</sup>

As far as we can ascertain, the arguments of Ingold et al. against CCH (either as the species responsible for the observed UV-vis absorptions or as an important species in this system) center on two themes (the remainder of their work is consistent with either interpretation).

**1. The Absence of Identical Correspondence to Weak Features (500–600 nm) Present in the Known UV-Vis Spectrum of Cyclohexadienyl Radical ( $\text{C}_6\text{H}_7^*$ ).**<sup>15</sup> However, interactions between the  $\pi$ -electrons and the out-of-plane C–H bonds are responsible for the visible bands in  $\text{C}_6\text{H}_7^*$ . The energetics of this interaction are likely to change drastically with the substitution of H by Cl. Further, the consequences of interaction of the C–Cl bond with the  $\pi$ -electrons on the spectrum, although unknown, nonetheless might be the source of the 490-nm band. Clearly, use of  $\text{C}_6\text{H}_7^*$  as a spectroscopic model provides little basis for eliminating CCH as the transient.

**2. The Lack of an Effect of Molecular Oxygen on the Rate of Disappearance of the Transient.** This was employed<sup>15</sup> with two assumptions: (a) a  $\pi$ -complex does not react with  $\text{O}_2$  (in accord with our basic assumption) and (b) CCH would react with  $\text{O}_2$  with a rate constant of  $>10^9 \text{ M}^{-1} \text{ s}^{-1}$ , just as cyclohexadienyl (an assumption we demonstrate is not correct).

Our results from the photochlorination of benzene in the presence of  $\text{O}_2$  indicate that CCH reacts with  $\text{O}_2$  at a rate less than one-sixth that of the  $\text{CCH}/\text{Cl}_2$  reaction. Utilizing our tentative rate constants (Table XII), we estimate that the rate for trapping of CCH by  $\text{O}_2$  is  $500\times$  slower than the rate for trapping of  $\text{C}_6\text{H}_7^*$ . An analogous retardation of the  $\text{O}_2$  reaction is reported for the 6-hydroxycyclohexadienyl radical.<sup>51</sup> Thus,

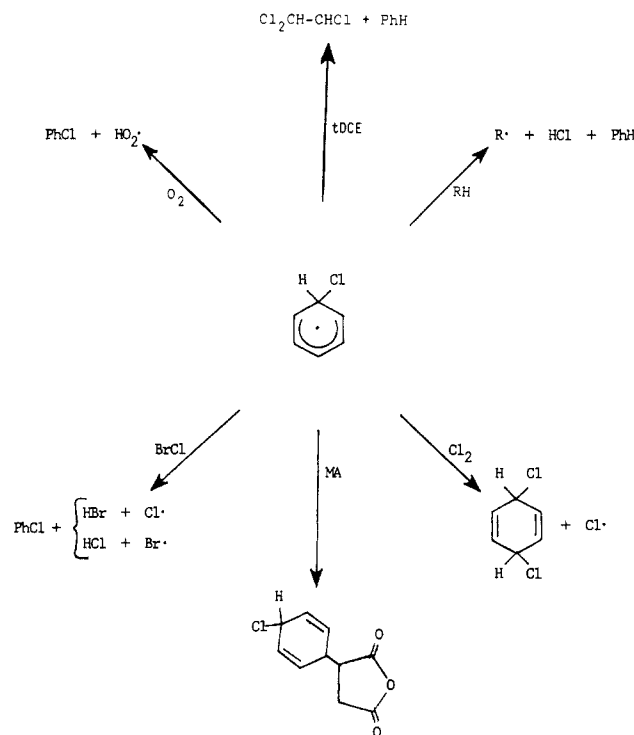
(51) ESR spectra of cyclohexadienyl radical substituted with electronegative substituents at the ipso position (e.g., 6-fluoro<sup>34,35</sup> and 6-hydroxy<sup>37</sup>) indicate a decrease of spin density at the out-of-plane hydrogen. Spin density at H is the obvious driving force for the reaction with  $\text{O}_2$ . Thus, there is no reason to expect that CCH would react with  $\text{O}_2$  as rapidly as  $\text{C}_6\text{H}_7^*$  does. The effect of replacement of H by Cl at C-6 should be a decrease in the rate of reaction with  $\text{O}_2$ . The 6-hydroxycyclohexadienyl radical has a hyperfine coupling constant to the out-of-plane H of  $36 \text{ G}^{37}$  ( $48 \text{ G}$  for  $\text{C}_6\text{H}_7^*$ <sup>36</sup>), and it reacts with  $\text{O}_2$  at a lower rate than  $\text{C}_6\text{H}_7^*$ . Further, in this instance the reactive site is not the out-of-plane hydrogen atom,<sup>43</sup> indicating the rate of reaction at the ipso site of  $\text{HOC}_6\text{H}_6^*$  must be less than  $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ;  $\text{HOC}_6\text{H}_6^* + \text{O}_2 \rightarrow \text{HOC}_6\text{H}_6\text{O}_2^*$  ( $k = 5.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>45</sup> Clearly, the failure to observe  $\text{O}_2$  quenching of the UV spectrum is a weak and unacceptable basis for excluding CCH as an intermediate.

(52) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095.

(53) If the  $\pi$ -complex assignment is correct, then what is the origin of the  $<330$ -nm absorption? One might guess that this is due to  $\pi\text{-}\pi^*$  transitions in the complexed benzene molecule. However, the UV spectrum of benzene consists of the following bands (molar absorptivity in parentheses): 184 (60000), 204 (7900), and 256 (200) nm.<sup>54</sup> The assignment of the  $<330$ -nm band to  $\pi\text{-}\pi^*$  transitions in the complexed benzene molecule would require one to postulate that the presence of  $\text{Cl}^*$  significantly perturbs the  $\pi$ -system of PhH. This "significant" perturbation might be better ascribed to the formation of a 6-chlorocyclohexadienyl radical, since the major band in the UV spectrum of  $\text{C}_6\text{H}_7^*$  occurs at 318 nm.<sup>43,44</sup>

(54) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 3rd ed.; Wiley: New York, 1974; p 248.

Scheme V



failure to observe  $\text{O}_2$  quenching provides no basis for excluding CCH from consideration as the species responsible for the observed UV-vis spectrum.

Thus, the structure and identity of the intermediate(s) in the  $\text{Cl}^*/\text{PhH}$  system are unsettled on the basis of spectroscopic evidence. Interaction of  $\text{I}^*$  or  $\text{Br}^*$  with  $\text{C}_6\text{H}_6$  results in the formation of  $\pi$ -complexes. The  $\text{Br}^*/\text{PhBr}$   $\pi$ -complex is reported to decay to the 6-bromocyclohexadienyl radical. The interaction of  $\text{F}^*$  with benzene produces only the 6-fluorocyclohexadienyl radical, with no evidence for the  $\text{F}^*/\text{PhH}$   $\pi$ -complex. On this basis, the intermolecular structures for the intermediates in the  $\text{PhH}/\text{Cl}^*$  system remains unsettled.

**D. The Chlorine Atom/Benzene System. Summary. 1. Synthetic Uses of Benzene-Mediated Photochlorinations.** For the photochlorination of DMB (and presumably, with appropriate statistical correction, any substrate containing  $3^\circ$  and  $1^\circ$  H's), the selectivity  $r(3^\circ/1^\circ)$  at any  $[\text{PhH}]$  or  $[\text{RH}]$  is predicted (standard deviation 7%) by eq 12.

$$r(3^\circ/1^\circ) = 6 \left\{ \frac{0.66 + 4.22[\text{PhH}] + 0.893[\text{RH}]}{1 + 0.203[\text{PhH}] + 1.35[\text{RH}]} \right\} \quad (12)$$

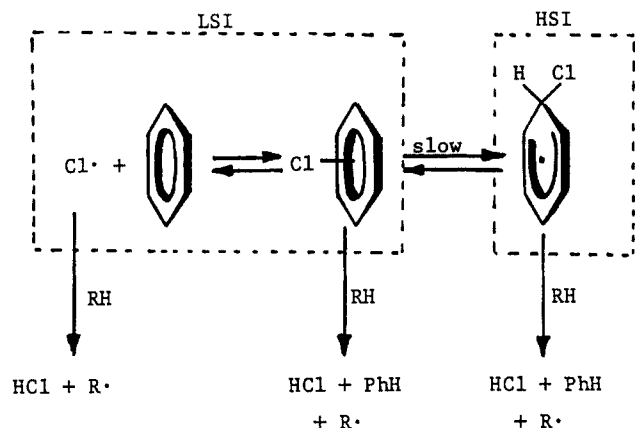
Maximal selectivity is attained at high arene concentrations and low RH concentrations. These considerations ensure that the HSI achieves its equilibrium concentration. Failure to recognize the relationship of  $[\text{RH}]$  to selectivity has undoubtedly led to disappointing results in benzene-moderated synthetic photochlorinations in the past.

Another factor in the  $\text{PhH}/\text{Cl}^*$  system is that the substrate must be sufficiently reactive with the HSI, having  $2^\circ$  or  $3^\circ$  C–H's, or more reactive functional groups. Primary hydrogens and the H's of  $\text{CH}_2\text{Cl}_2$  are less reactive toward the HSI. For the HSI, the following reactivity order is found:  $3^\circ \text{H}$  (130)  $>$   $2^\circ \text{H}$  (27)  $>$   $1^\circ \text{H}$  [1.0]. (For  $\text{Cl}^*$ , the reactivity order is  $3^\circ \text{H}$  (4.0)  $>$   $2^\circ \text{H}$  (3.5)  $>$   $1^\circ \text{H}$  [1.0].)<sup>3</sup> A substrate composed solely of hydrogens equally or less reactive than  $1^\circ$  H's is likely to react exclusively with the small amount of the LSI and not with the HSI.

Thus, although parameters have been defined so as to provide predictability in selective photochlorination of substrates, the procedure has a limited scope of applicability, and a need still exists for a more practical method of carrying out selective chlorinations.

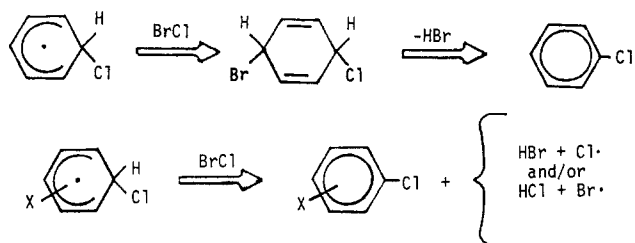
**2. CCH in the Chlorine Atom/Benzene System.** The descriptive chemistry of the CCH can be summarized as follows (Scheme

Scheme VI



V). (a) Alkanes with 2° or 3° H's react with the CCH to make alkyl radicals, HCl, and PhH. (b) Alkenes, react with CCH, yielding the  $\beta$ -chloroalkyl radicals and PhH. (c) CCH adds to the double bond of maleic anhydride. (d)  $\text{Cl}_2$  reacts with the CCH to make dichlorocyclohexadienes. (e)  $\text{O}_2$  reacts with the CCH to make chlorobenzene and  $\text{HO}_2^\cdot$ . (f)  $\text{BrCl}$  reacts with the CCH to form  $\text{PhCl}$  and  $\text{HBr} + \text{Cl}^\cdot$  (or  $\text{HCl} + \text{Br}^\cdot$ ).<sup>55</sup> To explain these properties, the CCH must possess the following structural features: radical character at Cl (required by a and b), radical character

(55) The major product of the photochlorination of benzene with  $\text{Cl}_2$  is  $\text{C}_6\text{H}_5\text{Cl}_6$ , indicating that the reaction of CCH with  $\text{Cl}_2$  at carbon (yielding  $\text{C}_6\text{H}_5\text{Cl}_2 + \text{Cl}^\cdot$ ) occurs more readily than reaction at the ipso H (yielding  $\text{PhCl} + \text{HCl} + \text{Cl}^\cdot$ ). In contrast, reaction of CCH with bromine chloride ( $\text{BrCl}$ ) exhibits a different regiochemistry: chlorobenzene is the major product (Skell, P. S.; Baxter, H. N., unpublished results). The  $\text{BrCl}$  substitution formally involves the loss of the ipso H from CCH. However, an abstraction/elimination process cannot be rigorously excluded.



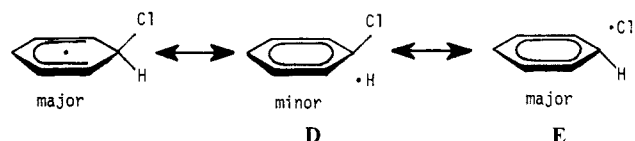
(56) The rate constants in Table XII are a self-consistent set which are highly satisfactory in reproducing DMB selectivities but are not as satisfactory in reconciling the yields of substitution products. Specifically, the observed  $\text{RCl}$  yields in the presence of added reagents are consistently higher than would be predicted on the basis of these rate constants. Undoubtedly, the rate constants for reaction of CCH with *trans*-DCE,  $\text{Cl}_2$ , and MA are high, perhaps by as much as a factor of 10. Consider the maleic anhydride results (Table X). If it is assumed (a) that CCH is relatively unreactive to 1° H's (i.e., all 1°  $\text{RCl}$  comes from the LSI) and (b) that the LSI has approximately the same DMB selectivity as free  $\text{Cl}^\cdot$  (0.66), the yield of 3°  $\text{RCl}_{\text{HSI}}$  (%) and the yield of  $\text{CCH-MA-Cl}$  (100% - yield of  $\text{RCl}$ ) can be calculated for each experiment in Table X. Data are given as  $[\text{MA}]$ , 3°  $\text{RCl}_{\text{HSI}}$  (%), and  $[\text{CCH-MA-Cl}]/[3^\circ \text{RCl}_{\text{HSI}}]$ : 0, 76, and 0; 0.1, 58, and 0.57; 0.48, 35, and 1.6; 1.7, 10, and 8.6. The rate constant ratio for trapping of CCH by MA vs. DMB can be computed from a plot of the product ratio vs.  $[\text{MA}]/[\text{RH}]$ , which yields a straight line whose slope,  $k_{\text{MA}}/k_{\text{RH}}$ , is 0.508 ( $R = 0.994$ ). In contrast, our quantitative treatment yields  $k_{\text{MA}}/k_{\text{RH}} = 2.4 \pm 0.9$ , in reasonably good agreement. It is worth noting that the quantitative analysis (supplementary materials) represents an ambitious undertaking, attempting to reconcile the interconversion of three intermediates ( $\text{Cl}^\cdot$ ,  $\pi\text{C}$ , and CCH) and their respective reaction pathways. The "cost" of this additional information is lower precision in estimating product yields. This treatment relates one dependent variable (DMB selectivity) to three independent variables ( $\text{PhH}$ , DMB, and T concentrations) and as many as eight adjustable parameters of which only two are independently known, the remainder being assumed or allowed to float. Consequently, we do not wish to imply that the values reported in Table XII are any more than estimates. However, we do believe that these "estimates" demonstrate that the proposed mechanism for the benzene-mediated photochlorination of DMB (Scheme III') is internally consistent and also consistent with the laser flash photolysis results for the kinetics for the HSI and free  $\text{Cl}^\cdot$ . The derived rate constants are reasonable with respect to all available literature precedent.

at carbon (required by c and d), and radical character at the ipso hydrogen (required by e and f).

A hybrid structure for CCH, consistent with known properties of other cyclohexadienyl radicals, accommodates these properties.

The  $<330\text{-nm}$  band is assigned to the CCH. Three unresolved possibilities must be considered for the assignment of 490 nm: (1) the 490-nm band may be wholly attributable to the  $\pi$ -complex, or the CCH also contributes to the 490-nm band by (2) enhancement of the 500–600-nm bands of  $\text{C}_6\text{H}_7^\cdot$  by chloro substitution (e.g., canonical structure D) or (3) from charge-transfer interactions of the C–Cl band (e.g., canonical structure E). In Appendix II we suggest further research activities which might help resolve this issue.

Canonical Structures for CCH



#### IV. Conclusion

All the evidence points strongly to the 6-chlorocyclohexadienyl radical (CCH) as an important intermediate in the  $\text{PhH}/\text{Cl}^\cdot$  system. Our major conclusions are summarized below. (1) Reactions of alkyl radicals with  $\text{Cl}_2$  in benzene produces only (or mainly) a low-selectivity intermediate (LSI) and not the HSI. (2) The low-selectivity intermediate is not the free chlorine atom. (3) The only (or major) path to the HSI is from the LSI. (4) The presence of reagents which react with CCH bring about a decrease in the steady-state concentration of the HSI. (5) A general criterion is provided to recognize those species which react with the HSI.

All the evidence is consistent with a mechanism which ascribes low-selectivity hydrogen abstractions to a mixture of the  $\pi$ -complex and free  $\text{Cl}^\cdot$  and high-selectivity hydrogen abstractions to the 6-chlorocyclohexadienyl radical. The crucial features of this mechanism are summarized in Scheme VI.

This mechanism avoids the assignment of HSI function to  $\pi\text{C}$  and thus brings in line the effects of benzene solvation on  $\text{Cl}^\cdot$ , so that, like other radicals, there is no discernible effect of solvation on reactivity.

#### V. Experimental Section

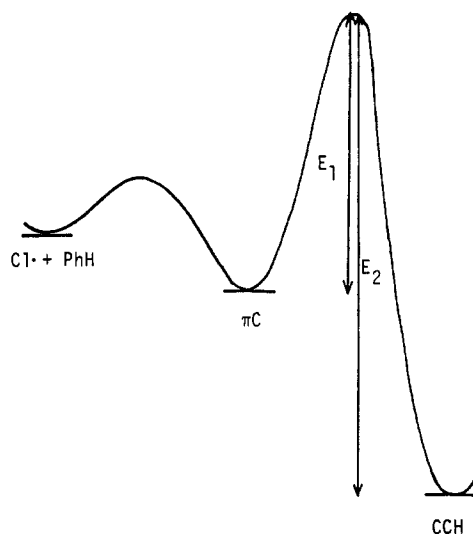
**General.**  $^1\text{H}$  NMR spectra (60 MHz) were recorded on a Varian EM-360 spectrometer with chemical shifts reported on the  $\delta$  scale relative to hexamethyldisiloxane ( $\delta$  0.07).

Gas chromatographic analyses were performed on one of the following instruments: a Varian 1200, a Varian 1400, or a Hewlett-Packard 5790A. Each GC was equipped with a DB-5 capillary column (30 m  $\times$  0.25 mm), an FID detector, and a HP3390A reporting integrator. In all cases, products were identified by comparison of the retention time to that of an authentic sample and quantitated vs. a measured quantity of an appropriate internal standard (utilizing a predetermined GLC sensitivity factor).

**Materials.** Benzene (Fisher) was purified by the following procedure. A flask containing benzene was cooled at  $-20^\circ\text{C}$  until it was ca. 75% solid. The supernatant was poured off and discarded. The solid benzene was allowed to melt at room temperature. The recrystallization was repeated and the resultant benzene stored over 4- $\text{\AA}$  molecular sieves. GLC analysis indicated purity  $\geq 99.9\%$ .

Bromine (Aldrich) was used without further purification. Carbon tetrachloride (Fisher) was used without further purification. Chlorine (Matheson, UHP) was transferred to a glass pressure tube, degassed, and stored at  $0^\circ\text{C}$ . The required amount of  $\text{Cl}_2$  was purified immediately before use by condensation from a trap at  $-78^\circ\text{C}$  directly into the reaction mixture (thereby eliminating  $\text{H}_2\text{O}$ ). Cyclohexane (Aldrich Gold Label) was used without further purification. (*E*)-1,2-Dichloroethene (Aldrich) was distilled and stored over 4- $\text{\AA}$  molecular sieves, purity  $>98\%$ . Dichlorosuccinic anhydride (*dl*/meso mixture) was prepared by the photoinitiated addition of  $\text{Cl}_2$  to maleic anhydride. 2,3-Dimethylbutane (Aldrich) was used without further purification. Maleic anhydride (Aldrich) was recrystallized twice from chloroform and dried for 1 h at high vacuum. *n*-Pentane (Aldrich Gold Label) was used without purification. Neopentane (Fluka) was used without further purification. Propane (Matheson, INST) was purified by the bromination of the olefin

Chart I



contaminants. A neat sample of propane was treated with  $\text{Br}_2$  for 30 min at  $0^\circ\text{C}$ . After unreacted  $\text{Br}_2$  was quenched with corn oil (Mazola),  $\text{C}_3\text{H}_8$  was distilled through two  $-78^\circ\text{C}$  traps and collected at  $-196^\circ\text{C}$ . By this procedure,  $\text{C}_3\text{H}_8$  of purity  $>99.9\%$  (GLC) was obtained.

Tetrachloroethene (Aldrich Gold Label) was used without further purification. Trichloroethene (Aldrich Gold Label, 99+%) was used without further purification. Trichlorofluoromethane (Pennwalt) was stored over 4-Å molecular sieves and used without further purification. 1,1,2-Trichlorotrifluoroethane (Aldrich Gold Label, 99+%) was used without further purification.

**Photochlorination of Alkanes.** All reactions were carried out in a 30-mL Pyrex pressure tube equipped with a Teflon-coated magnetic stirbar and a Teflon needle valve. Reactant mixtures were degassed (prior to the addition of  $\text{Cl}_2$ ) 3 to 4 times by the freeze-pump-thaw method (freezing to  $-196^\circ\text{C}$  and thawing at room temperature). Molecular chlorine was added. The sealed pressure tube was placed in a water bath maintained at  $20^\circ\text{C}$  and irradiated (with stirring) through two layers of Pyrex with a 75-W tungsten lamp at a distance of 10 cm.

**A. Dilute  $\text{Cl}_2$ .** In a typical experiment, the desired quantities of liquid or solid reagents were combined, and the resulting solution (volume  $\sim 10$  mL) was transferred to a sealed pressure tube. Gaseous reagents were measured manometrically and condensed into the pressure tube via a vacuum line.

A calibrated gas pipet was connected to a pressure tube containing  $\text{Cl}_2$  (ca. 3 atm at  $0^\circ\text{C}$ ). The volume was evacuated, the pipet was closed, and molecular  $\text{Cl}_2$  was allowed to expand into the evacuated volume. The pipet was opened so as to allow the excess chlorine to escape and bring the contents to ambient pressure. The measured  $\text{Cl}_2$  was condensed into a trap (vac-line), degassed, and from the trap at  $-78^\circ\text{C}$  was subsequently condensed into the pressure tube.

The pressure tube was sealed, placed in a thermostatically maintained water bath, and irradiated. Reaction times of 2–30 min were employed, depending on the nature of the reaction (see tables).

The reaction mixtures were analyzed by one of the following procedures. (1) A measured amount of an appropriate internal standard was added and the reaction mixture analyzed directly by GLC. In instances where the hexachlorobenzene yield was determined, the volatile materials (everything except  $\text{C}_6\text{H}_6\text{Cl}_6$ ) were removed by a high-vacuum trap-to-trap distillation at room temperature. (2) The nonvolatile material ( $\text{C}_6\text{H}_6\text{Cl}_6$ ) was quantitated by  $^1\text{H}$  NMR (vs. hexamethyldisiloxane). After addition of an internal standard, the volatiles were analyzed by GLC.

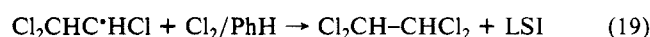
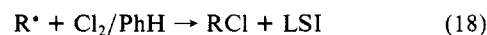
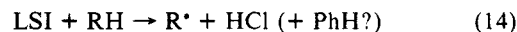
**B. Concentrated  $\text{Cl}_2$ .** The procedure was the same as above with the following exceptions. (1)  $\text{Cl}_2$  was measured by liquid volume at  $0^\circ\text{C}$ . (2) Reaction mixtures were rigorously protected from incident light. (3) Irradiations were accomplished with a 75-W tungsten lamp through two Pyrex layers at a distance of 4 m. (4) After irradiation, excess  $\text{Cl}_2$  was quenched with either corn oil or propene, an appropriate internal standard added, and the reaction mixture analyzed by GLC.

**Acknowledgment.** Financial support from the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged with gratitude. We thank R. S. Morbeto for assistance in preparing this manuscript.

## Appendix I. Effects of Alkane Concentration and Added Reagents on the LSI/HSI Ratio

To fully understand the effects of alkane concentration and added reagents on the LSI/HSI ratio, consider the simplified mechanism depicted in Scheme VII. Although *trans*-1,2-dichloroethene (*trans*-DCE) is assumed to be the added reagent, the arguments that follow are applicable to *any* reagent which can react with either the LSI or HSI.

### Scheme VII



With the steady-state approximation

$$\frac{d[\text{HSI}]}{dt} = 0 = k_{13}[\text{LSI}] - k_{-13}[\text{HSI}] - k_{15}[\text{HSI}][\text{RH}] - k_{17}[\text{HSI}][\text{trans-DCE}] \quad (20)$$

and solving for  $[\text{LSI}]/[\text{HSI}]$

$$\frac{[\text{LSI}]}{[\text{HSI}]} = \frac{k_{-13} + k_{15}[\text{RH}] + k_{17}[\text{trans-DCE}]}{k_{13}} \quad (21)$$

or

$$[\text{LSI}]/[\text{HSI}] = K_{13}^{-1} + (k_{15}/k_{13})[\text{RH}] + (k_{17}/k_{13})[\text{trans-DCE}] \quad (22)$$

Several critical features of the LSI/HSI equilibrating system emerge from this analysis. (1) In the absence of added reagents ( $[\text{trans-DCE}] = 0$ ) and at low alkane concentration ( $k_{15}[\text{RH}] < k_{-13}$ ), eq 21 can be reduced to eq 23. It becomes apparent that when  $[\text{RH}]$  is sufficiently low, the LSI and HSI are at equilibrium.

$$\frac{[\text{LSI}]}{[\text{HSI}]} = \frac{k_{-13}}{k_{13}} = K_{13}^{-1} \quad (23)$$

(2) At *any* concentration of alkane, eq 21 reveals that the presence of an added reagent (*trans*-DCE) perturbs the LSI/HSI ratio *only* if the reagent reacts with the HSI (i.e., the LSI/HSI ratio is independent of  $k_{16}$ ). (3) Inspection of eq 22 reveals that increased concentrations of alkane, or the presence of reagents which consume the HSI, perturb the LSI/HSI ratio to a higher-than-equilibrium value.

### Appendix II. Suggestions for Further Work

We suggest that the species responsible for the  $<330$ - and the  $490$ -nm bands in the  $\text{PhH}/\text{Cl}^*$  system should be unambiguously identified.

Laser flash photolysis studies of compounds such as 1,4-dichlorocyclohexadiene (DCCH) might indicate the sequential relation between CCH and  $\pi\text{C}$ . If the 6-chlorocyclohexadienyl radical could be produced directly, perhaps from reaction of DCCH with  $\text{R}_3\text{Sn}^*$ , our interpretation would predict that the observed UV spectrum be identical with that produced from  $\text{PhH} + \text{Cl}^*$ . If one makes the reasonable assumption that the 6-chlorocyclohexadienyl radical is the lowest energy intermediate in the  $\text{PhH}/\text{Cl}^*$  system, the Ingold rationale<sup>15</sup> (that CCH is a negligible component of the  $\text{PhH}/\text{Cl}^*$  system because the conversion  $\pi\text{C} \rightarrow \text{CCH}$  is slow) carries with it as a corollary that *the conversion  $\text{CCH} \rightarrow \pi\text{C}$  is slower ( $E_1 < E_2$ , Chart I).*

Thus, the Ingold rationale would predict that the transient produced by using DCCH as a precursor would have, both initially and ultimately, a different UV spectrum and different reaction

kinetics from the transient observed in the PhH/Cl<sup>+</sup> system. On the other hand, if only the <330- and 490-nm bands are found at the earliest times, it would be proof that the spectrum must be attributed to the CCH.

A second crucial test would result from examination of the C<sub>6</sub>H<sub>6</sub>/Cl<sup>+</sup> system in the picosecond regime with high arene concentrations, in a manner similar to what was done in the iodine atom studies.<sup>25,26</sup> This might help answer questions regarding simultaneous or sequential appearance of the <330- and 490-nm bands and provide a rate constant for formation of the chlorine atom/benzene  $\pi$ -complex which would be applicable where the Cl atom is generated in contact with benzene molecules.

The existence of Br atom or I atom  $\pi$ -complexes with arenes appears well documented.<sup>47</sup> We have provided evidence which suggests that the complex formed between a Cl atom and a benzene molecule is the 6-chlorocyclohexadienyl radical. For fluorine, the spectroscopic evidence is solely for the 6-fluorocyclohexadienyl radical.<sup>38</sup> There appears to be a gradation from

relatively weak interactions, i.e., I<sup>+</sup> and arene (best viewed as a  $\pi$ -complex), to stronger covalent interactions (best viewed as a 6-halocyclohexadienyl radical or  $\sigma$ -complex) in the series I  $\rightarrow$  F. This transition from the  $\pi$ - to  $\sigma$ -complex should be accompanied by (1) an alteration of angle between the carbon-halogen bond and the plane of the benzene ring (from 90° when X = I to 120° when X = F) and (2) a decrease in the C-X bond length. We bring this hypothesis to the attention of theoreticians.

**Registry No.** DMB, 79-29-8; MA, 108-31-6; CCH, 67542-83-0; PhH, 71-43-2; D<sub>2</sub>, 7782-39-0; (E)-ClCH=CHCl, 156-60-5; Cl<sub>2</sub>C=CHCl, 79-01-6; Cl<sub>2</sub>C=CCl<sub>2</sub>, 127-18-4; pentane, 109-66-0; 2,4-dimethylpentane, 108-08-7; cyclohexane, 110-82-7; neopentane, 463-82-1; propane, 74-98-6.

**Supplementary Material Available:** Quantitation of the effects of variations in [DMB], [PhH], and [T] and a table of least-squares analysis of data (9 pages). Ordering information is given on any current masthead page.

## Stereoelectronic Effects in the Hydrolysis of Bicyclic and Acyclic Phosphates and Phosphorothionates

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**Abstract:** The bicyclic phosphate OP(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>3</sub> (**1**) hydrolyzes  $5.2 \times 10^3$  times faster than the acyclic compound OP(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> at pH 14. At the same pH the bicyclic phosphorothionate SP(OCH<sub>2</sub>)<sub>3</sub>CCH<sub>3</sub> (**2**) hydrolyzes  $8.1 \times 10^2$  times faster than the acyclic compound SP(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>. Part of this rate enhancement is attributed to a stereoelectronic factor since compounds **1** and **2** have two lone pairs antiperiplanar (app) to the breaking P-O bond, while in order to place two lone pairs app to the breaking P-O bond in the acyclic compounds, the molecule must be constrained to an appropriate conformation which is disfavored entropically. The anion <sup>-</sup>O<sub>2</sub>P(OCH<sub>2</sub>)<sub>2</sub>CCH<sub>3</sub>(CH<sub>2</sub>OH) (**3**), which is the base hydrolysis product of **1**, was identified by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy. Its derivatives HO<sub>2</sub>P(OCH<sub>2</sub>)<sub>2</sub>CCH<sub>3</sub>(CH<sub>2</sub>OH) (**4**), the diastereomeric ester MeO<sub>2</sub>P(OCH<sub>2</sub>)<sub>2</sub>CCH<sub>3</sub>(CH<sub>2</sub>OH) (**5a,b**), and the diastereomeric ether-ester MeO<sub>2</sub>P(OCH<sub>2</sub>)<sub>2</sub>CCH<sub>3</sub>(CH<sub>2</sub>OCH<sub>3</sub>) (**6a,b**) were isolated and characterized by <sup>1</sup>H and <sup>13</sup>C NMR and by mass spectroscopies. The anion <sup>-</sup>O(S)P(OCH<sub>2</sub>)<sub>2</sub>CCH<sub>3</sub>(CH<sub>2</sub>OH) (**7**), which is the base hydrolysis product of **2**, is shown to be a single isomer by the <sup>1</sup>H NMR spectrum of its neutral ester derivative, CH<sub>3</sub>S(O)P(OCH<sub>2</sub>)<sub>2</sub>CCH<sub>3</sub>(CH<sub>2</sub>OH), obtained via methylation of the acid **8** with diazomethane. The 2-oxo and 5-methyl substituents of **7** are cis to one another as is strongly suggested by the structural determination of the acid derivative **8** of **7** by X-ray means. These results are consistent with apical OH<sup>-</sup> attack on phosphorus followed by apical departure of an alkoxy oxygen.

In one of our laboratories it was shown through ab initio molecular orbital calculations<sup>2-8</sup> and experimentally<sup>9-14</sup> that kinetic

stereoelectronic effects<sup>15-19</sup> may play important roles in the reactions of organophosphorus compounds. In phosphate esters, these stereoelectronic effects involve facilitating the cleavage of

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