In order to obtain insight into the guest selectivity, we determined the K for cationic 6 and anionic 7 using a spectroscopic method. As shown in Figure 3,  $OD_{464}$  for Methyl Orange (7) decreased upon addition of 3 but was unchanged after addition of 5. This suggests that cationic 3 includes anionic 7. It is also seen from Figure 3 that 3 forms a 1:1 complex with 7 ( $K \approx 7.1 \times 10^4$  M<sup>-1</sup>). The reverse situration was found for cationic 6, which was selectively complexed by anionic 5 (K = 750 M<sup>-1</sup>). The results indicate that hydrophobic forces may be generally operative for complex formation in an aqueous system, but the selectivity is crucially governed by the electrostatic force.

The foregoing results demonstrate that *p*-(chloromethyl)calixarene is a useful intermediate to prepare new water-soluble calixarenes and that the charge on the calixarene cavity plays a crucial role in the guest selectivity. Further applications of these water-soluble calixarenes are currently under investigation in this laboratory.

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## Free-Radical Alkylations of Enones Involving Proton Transfers<sup>1</sup>

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Summary: Radical chain alkylations of the  $S_{RN}$ -type are described that involve the abstraction of a proton from intermediate adduct radicals to form radical anions capable of chain propagation by electron transfer to alkylmercury halides. Vinylic  $S_{RN}$  processes are described for *o*- and *p*-hydroxycinnamic acids in basic solution.

Sir: Photostimulated chain reactions of alkylmercury chlorides with many  $\alpha,\beta$ -unsaturated ketones, esters, lactones, and amides occur readily in the presence of iodide ion.<sup>2,3</sup> In these reactions the regioselectively formed  $\beta$ adduct enolyl radicals are reduced to the enolate anions by  $I^-/RHgI_2^-$  in processes which regenerate  $R^{\bullet,2}$  A similar reaction yielding the additive (reductive) alkylation product is observed with other anions, such as HO<sup>-</sup> or  $Me_3CO^-$ , which can form ate complexes with the mercurial (Table I). On the other hand,  $\alpha,\beta$ -unsaturated compounds such as coumarin react with alkyl radicals by  $\alpha$ -attack to generate the benzylic radical, which reacts slowly or not at all with RHgCl. However, a chain reaction can still be achieved because the adduct radical has an acidic  $\alpha$ -hydrogen atom. Addition of DABCO in Me<sub>2</sub>SO gives rise to substitutive (oxidative) alkylation to form 3-tert-butylcoumarin in 90% yield by the mechanism of Scheme I. Loss of a proton from 1 generates a powerful reducing species ( $E_0 = -1.6$  V) which continues the chain by electron transfer to RHgCl ( $E_0$  values for a variety of alkylmercury acetates in MeOH/H<sub>2</sub>O are  $\sim -0.2$  V).<sup>4</sup> In the absence of base, little reaction is observed while in the presence of KI or  $KI/K_2S_2O_8$  a complex reaction mixture is formed which includes the coupling product of 1 with a second t-Bu<sup>\*</sup>, 3-tert-butyldihydrocoumarin, a small amount of 3-tert-butylcoumarin, and four (two major and two minor) diastereomeric dimerization products of 1. A similar product distribution but with one of the diastereomers predominating was observed from the reaction with (t-Bu)<sub>2</sub>Cu(CN)Li<sub>2</sub> in THF at -78 °C in a process which ap-

 
 Table I. Photostimulated Reactions of t-BuHgCl with Enones in Me<sub>2</sub>SO

		% alkylation	
substrate	conditions <sup>e</sup>	sub- stitutive	additive
PhCOCH=CHCOPh	24 h <sup>b</sup>	tr	10°
PhCOCH=CHCOPh	24 h, KI	0	18°
PhCOCH=CHCOPh	2.5 h, KOH	0	32°
PhCOCH=CHCOPh	17 h, KI, K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	tr	76°
PhCOCH-CHCOPh	PhH, 24 h <sup>b</sup>	tr	<b>4</b> <sup>c</sup>
PhCOCH—CHCOPh	PhH, 4 h, 2 equiv of t-BuOK	0	52°
(Z)-EtO <sub>2</sub> CCH=CHCO <sub>2</sub> Et	20 h <sup>b</sup>	0	37 <sup>d,e</sup>
(Z)-EtO <sub>2</sub> CCH=CHCO <sub>2</sub> Et	3 h, KI	0	100 <sup>d</sup>
(Z)-EtO,CCH-CHCO,Et	3 h. Na <sub>2</sub> SO <sub>4</sub> <sup>b</sup>	0	70 <sup>d,e</sup>
(Z)-EtO <sub>2</sub> CCH=CHCO <sub>2</sub> Et	i PrHgČl, 17 h	0	43 <sup>e√</sup>
Z)-EtO2CCH=CHCO2Et	i-PrHgCl, 3 h, KI, $K_{2}S_{2}O_{3}^{h}$	0	82 <sup>f</sup>
(Z)-EtO,CCH-CHCO,Et	PhH, 20 h <sup>b</sup>	0	48 <sup>d,e</sup>
(Z)-EtO <sub>2</sub> CCH—CHCO <sub>2</sub> Et	PhH, 20 h, DABCO <sup>b</sup>	0	65 <sup>d,e</sup>
CH <sub>2</sub> =CHCOPh	13 h, DABCO <sup>b</sup>	tr	1100
CH <sub>2</sub> =CHCOPh	18 h, NaI	0	57°.s
CH <sub>2</sub> =CHCOPh	18 h, KI, $K_2S_2O_8^h$	0	86**
coumarin	24 h <sup>b</sup>	tr	tr
coumarin	12 h, DABCO	90 <sup>i</sup>	tr

<sup>a</sup> Reaction of ~0.5 M substrate with 4 equiv of t-BuHgCl and 4 equiv of specified reagents under irradiation from a 275-W fluorescent sunlamp at ~40 °C. Workup with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. <sup>b</sup> Unreacted substrate recovered. <sup>c</sup>t-BuCH(COPh)CH<sub>2</sub>COPh. <sup>d</sup>t-BuCH(CO<sub>2</sub>Et)CH<sub>2</sub>CO<sub>2</sub>Et. <sup>e</sup>Significant amounts of a 2:1 telomer formed. <sup>f</sup>i-PrCH(CO<sub>2</sub>Et)CH<sub>2</sub>CO<sub>2</sub>Et. <sup>e</sup>t-BuCH<sub>2</sub>CCPh. <sup>h</sup>2 equivalents. <sup>i</sup>3-tert-Butylcoumarin.

Scheme I



parently also proceeds by the intermediacy of 1. The persulfate/iodide system rapidly forms t-Bu<sup>•</sup> by the attack of I<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> upon t-BuHgCl as evidenced from CIDNP

<sup>(1)</sup> Electron Transfer Processes. 48. This work was supported by the National Science Foundation (Grant 8717871) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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 $\frac{1 + g x}{1 + g^0} = RC(R^2) = CHCOR^1 \quad (3)$ 

 $R = aikyi; R^1 = aikyi, aryi, aikoxy; R^2 = hydrogen, R^1CO$ 

signals for Me<sub>2</sub>C=CH<sub>2</sub> and Me<sub>3</sub>CH formed by the diffusive encounter of two t-Bu<sup>•</sup> in the absence of a radical trap.<sup>3</sup> With  $\alpha,\beta$ -unsaturated systems leading to enolyl radicals, the I<sup>-</sup>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system leads cleanly to reductive alkylation products ( $h\nu$ , Me<sub>2</sub>SO) such as t-BuCH<sub>2</sub>CH<sub>2</sub>COPh (86%), t-BuCH(CO<sub>2</sub>Et)CH<sub>2</sub>CO<sub>2</sub>Et (87%), and t-BuCH(COPh)CH<sub>2</sub>COPh (76%), Table I.

With t-BuHgCl/KOH/ $h\nu$  in Me<sub>2</sub>SO, coumarin reacts to give a mixture of 3-tert-butylcoumarin (Scheme I) and (E)-o-HOC<sub>6</sub>H<sub>4</sub>CH—CHCMe<sub>3</sub>. o-Hydroxycinnamic acid under the same conditions yields the decarboxylated alkene in 50% (Me<sub>2</sub>SO) to 60% (DMF) upon photolysis. This reaction apparently involves a vinylic S<sub>RN</sub> process<sup>5</sup> (Scheme II) followed by decarboxylation. Cinnamic acid fails to react, but p-hydroxycinnamic acid yields p-HOC<sub>6</sub>H<sub>4</sub>CH—CHCMe<sub>3</sub> in 60% (Me<sub>2</sub>SO) to 70% (DMF).

Another example of activation of an intermediate adduct radical by proton transfer is observed in the photostimulated reaction of PhCOCH<sub>2</sub>HgCl or (PhCOCH<sub>2</sub>)<sub>2</sub>Hg with norbornene. Here the intermediate adduct radical cyclizes and ionizes in Me<sub>2</sub>SO to yield the ketyl. The chain is continued by electron transfer to the mercurial with the  $\alpha$ -tetralone derivative formed in 50–70% yield (reaction 1). Traces of a dihydro derivative are eliminated by including DABCO in the system or by oxidation of the crude reaction product.



The photostimulated reaction of (Z)-EtO<sub>2</sub>CCH= CHCO<sub>2</sub>Et with t-BuHgCl (Table I) forms only the reductive alkylation product in the presence or absence of I<sup>-</sup> or DABCO (reaction 2 of Scheme III). With t-BuHgCl, reductive alkylation is general for simple enolyl radicals even in the presence of bases, possibly because complexation of nucleophiles increases the reactivity of the mercurial in reaction 2. However, with *i*-PrHgCl, which reacts more slowly with electrophilic radicals,<sup>6-8</sup> competition can

 Table II. Photostimulated Reactions of t-BuHgCl with

 1,4-Naphthoquinone in Benzene

		% yield	
conditions <sup>a</sup>	2	3	
15 h	39	14	
15 h, 4 vol % H <sub>2</sub> O	0	74	
16 h, 4 vol % HOAc	0	78	
17 h, 4 equiv of $(NH_4)_2S_2O_8$	0	95	
24 h, 8 equiv of NaI	9	52	
24 h, 2 equiv of DABCO	41-47	0	
28 h, 2 equiv of $K_2S_2O_8$ , 1.2 equiv of DABCO	47	0	
Me <sub>2</sub> SO, 17 h	6	0	
$Me_2SO$ , 19 h, 4 equiv of $(NH_4)_2S_2O_8$ , $NaI^b$	35	0	

<sup>a</sup>Reaction of 0.5 mmol of 1,4-naphthoquinone with 4 equiv of t-BuHgCl in 12 mL of solvent with 275-W fluorescent sunlamp irradiation at 40 °C. <sup>b</sup>In room light at 25 °C.



be observed between  $S_H^2$  attack of the adduct radical at the mercury atom (reaction 2) and loss of a proton from the adduct radical (reaction 3). Photostimulated reactions in the absence of base gave upon workup only the saturated alkylation product (with or without I<sup>-</sup>, Table I), but in the presence of 4 equiv each of *i*-PrHgCl and DABCO, the unsaturated alkylation product predominated ((*Z*)-*i*-PrC(CO<sub>2</sub>Et)=CHCO<sub>2</sub>Et/*i*-PrCH(CO<sub>2</sub>Et)CH<sub>2</sub>CO<sub>2</sub>Et = 3/1). Under similar conditions, *n*-BuHgCl gave only BuCH(CO<sub>2</sub>Et)CH<sub>2</sub>CO<sub>2</sub>Et with I<sup>-</sup>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> but only BuC-(CO<sub>2</sub>Et)=CHCO<sub>2</sub>Et with DABCO.

With quinones the adduct radicals are more acidic and competition between reactions 2 and 3 could be observed with t-BuHgCl. The free radical tert-butylation of 1,4naphthoquinone by t-BuHgCl can be controlled to give either the substitutive (2) or the additive (3) product by the proper choice of proton donor/acceptor. Photolysis



in PhH leads to a mixture where 3 exists completely in the diketone form (<sup>1</sup>H NMR, IR). In PhH (Table II), reactions leading exclusively to 3 are observed in the presence of proton donors such as  $H_2O$ , HOAc, or  $(NH_4)_2S_2O_8$ . The mixture of products observed in PhH without a proton

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<sup>(8)</sup> The relative reactivities of t-BuHgCl, i-PrHgCl, and n-BuHgCl are 1.0:0.07:0.014 toward RCH<sub>2</sub>CHP(O)(OEt)<sub>2</sub> and 1.0:0.08:<0.003 toward PhS<sup>+</sup>: Russell, G. A. NATO ASI Series C 1989, 257, 13.

donor is apparently due to semiquinone formation (Scheme IV). As predicted from Scheme IV, addition of a base such as DABCO causes the reaction product to change completely, and only the substituted quinone 2 is formed in a slow reaction because of the poor driving force for the transfer of an electron from  $2^{\bullet-}$  ( $E_0 \sim 0$ ) to t-BuHgCl. Only 2 is observed in Me<sub>2</sub>SO, albeit in low yield. Substitutive (oxidative) free radical alkylations of quinones by tert-alkyl iodides has also been described in the systems

 $\rm RI/H_2O_2/Fe(II)/Me_2SO, RI/t-BuOOH/Fe(III), RI/H_2O_2/Me_2CO/H^+, and RI/CH_3CO_2^-/S_2O_8^{2-}/H_2O.^9 It has also been demonstrated that the reaction of trialkylboranes with 1,4-quinones to form upon hydrolysis the 2-alkyl-hydroquinones proceeds by a free-radical chain mechanism.^{10}$ 

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## Observation of AlCl<sub>3</sub>-Catalyzed Trialkylsilylation of Benzene and Toluene with Chlorotrialkylsilanes in the Presence of Hünig Bases<sup>1</sup>

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Summary: AlCl<sub>3</sub>-catalyzed trialkylsilylation of benzene and toluene has been shown to occur using chlorotrialkylsilanes in the presence of Hünig bases.

Sir: Electrophilic silvlation of aromatic compounds such as benzene and toluene under typical Friedel-Crafts alkylation conditions using halosilanes and a Lewis acid catalyst has never been observed.<sup>2</sup> This is probably due to the great ease of protodesilvlation of any arylsilane formed under the reaction conditions (i.e., the protodesilvlation rate  $k_{-1}$  is faster than that of silvlation  $k_1$ , i.e.,  $k_{-1} > k_1$ ) as has been confirmed by the work of Eaborn<sup>3</sup> and Szele.<sup>4</sup> On the other hand, some examples of direct electrophilic silvlations of nonbenzenoid, highly activated aromatic systems such as ferrocene<sup>5</sup> and pyrrole<sup>6</sup> have been reported.

$$H + R_3 SiCI \xrightarrow{AICl_3} H + R_3 SiR_3 + HX: AICl_3$$

One way we considered for achieving silvlation of benzene or toluene is to slow down the rate of protodesilvlation by trapping the proton eliminated in the silylation reaction by a suitable hindered base. Following this strategy we now report observation of the direct silylation of benzene and toluene with a series of chlorotrialkylsilanes under Friedel-Crafts conditions in the presence of Hünig bases (hindered tertiary amines) as proton acceptors. When excess benzene or toluene was heated with chlorotrialkylsilane and aluminum trichloride in the presence of diisopropylethylamine at 150 °C in a sealed heavy walled glass tube for 24 h, the corresponding aryltrialkylsilanes were obtained in low, but detectable

Table I.	Trialkylsilylation	of Benzene	and Toluene
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substr	$R'_{3}SiCl, R' =$	yield,ª %	o:m:p
R = H	CH <sub>3</sub>	0.3	
R = H	CH <sub>2</sub> CH <sub>3</sub>	1.2	
R = H	$CH(CH_3)_2$	1.6	
$R = CH_3$	CH3	1.0	0.6:34.6:64.8

 $^{\rm a}$ Based on silylating agent; GC yields, calibrated by internal standards.

amounts. The mole ratio of R<sub>3</sub>SiCl:AlCl<sub>3</sub>:base was generally 1:4:2. The reaction mixture was worked up by quenching with aqueous NaHCO<sub>3</sub> followed by extraction with hexane. The product arylsilanes were identified by  $GC/MS^7$  and the yields were determined by  $GC^8$  using internal standards. The authentic compounds used for comparison were prepared according to literature methods.<sup>9</sup> In the case of trimethylsilylation the reaction was performed on a preparative scale with the isolation of the aryltrimethylsilanes and characterization by NMR, IR, and mass spectrometry.<sup>7,8,10</sup> The yield of trimethylsilylation of benzene was 0.3%, whereas that of toluene was 1%. The related triethylsilylation of benzene gave a 1.2% yield and triisopropylsilylation 1.6%. Although these yields, based on the amount of starting trialkylchlorosilanes, are too low to be considered of preparative value, it should be pointed out that the trialkylchlorosilanes under the reaction conditions undergo substantial disproportionation in the presence of AlCl<sub>3</sub> as the major reaction, explaining in part the low yields. Regardless, the first observation of electrophilic trialkylsilylation of benzene and toluene is significant both in regard of extending our knowledge of

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<sup>(10) (</sup>a) NMR spectra were obtained on a Varian Associates Model VXR-200 NMR spectrometer equipped with a 5-mm  $^{1}H/^{19}F$ -broad band probe. IR spectra were obtained on a Perkin-Elmer 1550 spectrometer. (b) We were unable to verify these results by subjecting the authentic isomers to the reaction conditions. Under these conditions the major reaction was protolytic desilylation. However, acid-catalyzed isomerizations of 1,2-bis(trimethylsilyl)benzenes have been reported, see ref 15.