Radical and Ionic Reactions of (Benzoylmethyl)mercurials[1]

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Photolysis of $PhCOCH_2HgCl$ or $(PhCOCH_2)_2Hg$ yields benzoylmethyl radicals which can be trapped by anions such as $Me_2C{=}NO_2^-$, $RC(CO_2Et)_2^-$, $RC(O^-){=}CH_2$ or by other electron-rich systems such as $(RO)_3P$, *N*-methylpyrrole, enamines, or norbornene. Electron transfer from the adduct radicals to the mercurial yields $PhCOCH_2A$ from the anions A^-, $PhCOCH_2P(O)(OR)_2$ from $P(OR)_3$, and the phenacyl derivative from *N*-methylpyrrole or enamines. Easily oxidized anions such as $PhCOCPh_2^-$ or $PhC(CH_3){=}NO_2^-$ react with $PhCOCH_2^\bullet$ by electron transfer to yield the dimer derived from the anion. Addition of $PhCOCH_2^\bullet$ to norbornene yields a substituted 3-benzoylpropyl radical which cyclizes at the ortho position of the benzoyl group to give the α-tetralone derivative.

Alkylmercury halides undergo photostimulated chain reactions of the S_{RN}-type with anions such as $CH_2{=}NO_2^-$ or $PhC(O^-){=}CH_2$ in which the adduct radical anions, e.g., $t\text{-}BuCH_2NO_2^{\bullet-}$ or $t\text{-}BuCH_2\dot{C}(O^-)Ph$, continue the chain by electron transfer to the alkylmercurial, a process which regenerates the alkyl radical.[2-5] In general, the rate of attack by the nucleophilic (electron-donating) *tert*-butyl radical decreases with electron-supplying substituents at the resonance-stabilized carbanionic center of the anion.[4,5] In a similar fashion, the reactivity of a variety of alkenes and alkynes toward the *tert*-butyl radical is greater with electron-withdrawing substituents than with electron-supplying substituents.[6]

Some examples of S_{RN}-type reactions (substitutions) have been observed in the photostimulated reactions of *t*-BuHgCl with neutral molecules, e.g. $CH_2{=}C(C_6H_4OMe\text{-}p)_2$.[7,8] However, to form an easily oxidized adduct radical capable of transferring an electron to RHgCl, an electron-rich substrate is required. In many cases such substrates have a low reactivity toward nucleophilic alkyl radicals because of the polar effect in radical addition reactions. [The polar effect, originally recognized in copolymerization reactions,[9] has been extended to numerous radical addition reactions of substituted alkenes[10] and heteroaromatics[11] of synthetic value. The rates and products of these and other radical reactions are often controlled by polar contributions to early transition states.[12]]

In the hope of extending the scope of S_{RN}-type substitutions using organomercurials as the radical source, we have investigated the photostimulated radical reactions of the (benzoylmethyl)mercurials since the benzoylmethyl radical is an electrophilic radical[13] and should add readily to electron-rich substrates. As predicted, the nucleophilic *tert*-butyl and electrophilic benzoylmethyl radicals display vastly different reactivities toward electron-rich substrates such as trialkyl phosphites, enamines, or *N*-methylpyrrole. These substrates have little reactivity toward $t\text{-}Bu^\bullet$ but readily trap $PhCOCH_2^\bullet$ to yield adduct radicals capable of transferring an electron to $PhCOCH_2HgCl$ or $(PhCOCH_2)_2Hg$ and thereby regenerate $PhCOCH_2^\bullet$.

Addition of $PhCOCH_2^\bullet$ to norbornene yields a carbon-centered radical which would not be expected to undergo electron transfer to $PhCOCH_2HgCl$. However, a chain reaction involving electron transfer can still be achieved by cyclization followed by the loss of a proton to yield an α-tetralone ketyl. Since the ketyl is a powerful reducing species ($E^\circ \sim -1.7$ v) electron transfer to the mercurial occurs readily with regeneration of $PhCOCH_2^\bullet$.

Table I. Photostimulated Reaction Products between $PhCOCH_2HgCl$ and Various Nucleophiles[a]

nucleophile[b]	time, h	products (% yield)[c]
$Me_2C{=}NO_2^-$	2	$PhCOCH_2CMe_2NO_2$ (22); $PhCOCH{=}CMe_2$ (65)
$MeCH{=}NO_2^-$	4	$PhCOCH_2CHMeNO_2$ (32); $PhCOCH{=}C(Me)NO_2$ (4)
$H_2C{=}NO_2^-$	5	$PhCOCH_2CH_2NO_2$ (3); O_2NCH_2HgCl; $PhCOCH_3$
$PhCH{=}NO_2^-$	3	$PhCOCH_2CH(Ph)NO_2$ (7); $PhCH{=}C(Ph)NO_2$ (48); $PhCH(NO_2)CH(NO_2)Ph$ (11)
$PhC(Me){=}NO_2^-$	3	$PhC(Me)(NO_2)C(Me)(NO_2)Ph$ (56); $PhC(Me){=}C(Me)Ph$ (13)
$EtC(CO_2Et)_2^-$	2	$PhCOCH_2C(Et)(CO_2Et)_2$ (70)
$MeC(CO_2Et)_2^-$	2	$PhCOCH_2C(Me)(CO_2Et)_2$ (61)
$HC(CO_2Et)_2^-$	6	$PhCOCH_2CH(CO_2Et)_2$ (27)
$PhC(CO_2Et)_2^-$	2	$PhCOCH_2CH(Ph)(CO_2Et)_2$ (21); $PhC(CO_2Et)_2C(CO_2Et)_2Ph$ (64)
$Me_3C(O^-){=}CH_2$	4	$PhCOCH_2CH_2COCMe_3$ (37)
$PhC(O^-){=}CMe_2$	2	$PhCOCH_2CMe_2COPh$ (52)
$PhC(O^-){=}CHMe$	4	$PhCOCH_2CH(Me)COPh$ (24)
$PhC(O^-){=}CHPh$	3	$PhCOCH(Ph)CH_2COPh$ (4); $PhCOCH(Ph)CH(Ph)COPh$ (63)
$PhC(O^-){=}CPh_2$	2	$PhCOC(Ph)_2C(Ph)_2COPh$ (71)
$Ph_2C{=}C{=}N^-$	2	$Ph_2C(CN)C(CN)Ph_2$ (69)

[a] Reactions performed in hexamethylphosphoric triamide under N_2 with photostimulation from a 275-W sunlamp ca. 15 cm from the Pyrex reaction flask. Reactions were performed on a 1-mmol scale with $[PhCOCH_2HgCl] = [N^-] = 0.1$ M. [b] Generated by the reaction of the conjugate acid with Me_3COLi. [c] Yields determined by integrated ^1H NMR with an internal standard and/or by GC analysis with biphenyl as the internal standard.

The present report describes these reactions and some of the complications resulting from competing ionic reactions of the (benzoylmethyl)mercurials and electron transfer reactions of the benzoylmethyl radical.

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Results and Discussion

Reactions with Anions. (Benzoylmethyl)mercurials are readily attacked at the mercury atom by nucleophiles such as I^-, $(EtO)_2PO^-$, or $CH_2{=}NO_2^-$ to generate $PhCOCH_3$ and mercury salt.[14] With some carbon-centered nucleophiles, a S_{RN} reaction has been observed (Scheme Ia),[15] but with benzylic anions an oxidative dimerization

Scheme I

(a) $A^- = Me_2C{=}NO_2^-$, $PhC(O^-){=}CH_2$

$$PhCOCH_2^\bullet + A^- \rightarrow PhCOCH_2A^{\bullet-}$$

$$PhCOCH_2A^{\bullet-} + PhCOCH_2HgCl \rightarrow PhCOCH_2A + PhCOCH_2HgCl^{\bullet-}$$

$$PhCOCH_2HgCl^{\bullet-} \rightarrow PhCOCH_2^\bullet + Hg^\circ + Cl^-$$

(b) $A^- = PhC(O^-){=}CPh_2$, $PhCH{=}NO_2^-$, Ph_2P^-

$$PhCOCH_2^\bullet + A^- \rightarrow PhCOCH_2^- + A^\bullet$$

$$A^\bullet + A^- \rightarrow A\text{-}A^{\bullet-}$$

$$A\text{-}A^{\bullet-} + PhCOCH_2HgCl \rightarrow A\text{-}A + PhCOCH_2^\bullet + Hg^\circ + Cl^-$$

process occurs according to Scheme Ib.[14] Table I summarizes the reaction products observed upon the photolysis of $PhCOCH_2HgCl$ in the presence of a variety of nucleophiles in HMPA. Similar reactions but in lower yields were observed in Me_2SO while in HMPA the presence of 18-crown-6 ether decreased the yield of the alkylation product.

Parts a and b of Scheme I both involve the reduction of $PhCOCH_2HgCl$ by one electron to form the enolyl radical which possesses a considerably different selectivity and reactivity than the *tert*-butyl radical in reactions with nucleophiles.[14] Thus, although *t*-Bu$^\bullet$ can be trapped by Ph_2P^- (to yield *t*-$BuPPh_2$ by a S_{RN} process), reaction of Ph_2P^- with $PhCOCH_2^\bullet$ leads to $Ph_2P\text{-}PPh_2$ via Scheme Ib.[16]

Electron transfer from adduct radical anions to simple alkylmercury halides occurs in a dissociative manner with a rate which increases with the stability of the incipient alkyl radical.[17,18] Electron transfer to $PhCOCH_2HgCl$ may involve $PhCOCH_2HgCl^{\bullet-}$ as an intermediate since radical ions such as $PhCOCH_2Br^{\bullet-}$ are known to exist and to undergo unimolecular elimination of Br^- with $k < 1 \times 10^6$ s^{-1} at ambient temperature in CH_3CN.[19] (p-$O_2NC_6H_4COCH_2Br^{\bullet-}$ decays with $k = 4 \times 10^4$ s^{-1} in H_2O and has a lifetime ~10 times greater than p-$O_2NC_6H_4CH_2Br^{\bullet-}$.[20])

Reactions with Trialkyl Phosphites. *tert*-Butylmercury chloride participates poorly in the photostimulated S_{RN} reaction with trialkyl phosphites. Reaction of $(RO)_3P$ with $PhCOCH_2HgCl$ occurred more efficiently (Scheme II), presumably because of a favorable polar effect

Scheme II (R = $PhCOCH_2$)

$$R^\bullet + (MeO)_3P \rightarrow R\dot{P}(OMe)_3 \quad (1)$$

$$R\dot{P}(OMe)_3 + RHgCl \rightarrow RP(OMe)_3^+ + RHgCl^{\bullet-} \quad (2)$$

$$RHgCl^{\bullet-} \rightarrow R^\bullet + Hg^0 + Cl^- \quad (3)$$

$$Cl^- + RP(OMe)_3^+ \rightarrow MeCl + RP(O)(OMe)_2 \quad (4)$$

Table II. Photostimulated Reaction of Alkylmercurials with $(MeO)_3P$[a]

mercurial (mmol)	mmoles of $(MeO)_3P$	$RP(O)(OMe)_2$,[b] %	$\frac{PhCOCH_2CH_2COPh}{PhCOCH_2P(O)(OMe)_2}$
t-BuHgCl (0.5)	2.5	<5	-
$PhCOCH_2HgCl$ (0.5)	0.5	30	1.10
$PhCOCH_2HgCl$ (0.5)	2.5	32	1.03
$PhCOCH_2HgCl$ (0.5)	10.0	37	0.81
$PhCOCH_2HgCl$ (0.25)	1.25	40	0.73
$PhCOCH_2HgCl$ (0.125)	0.625	44	0.57
$PhCOCH_2HgCl$ (0.125)	2.5	42	0.60
$PhCOCH_2HgCl$ (0.5)	2.5[c]	33[c]	0.97[c]
$(PhCOCH_2)_2Hg$ (0.5)	2.5	48	1.46

[a] Photolysis for 8 h in Rayonet 350-nm photoreactor in 5 mL of Me_2SO. [b] GC yield, mol of $RP(O)(OMe)_2$/mol of mercurial. [c] $(EtO)_3P$ yielding $PhCOCH_2P(O)(OEt)_2$.

in the addition step (reaction 1) and a more favorable driving force for the electron transfer of reaction 2. Table II summarizes some pertinent experimental observations. The reaction of (benzoylmethyl)mercurials with trialkyl phosphites represents a simple route to (benzoylmethyl)phosphonates via an Arbuzov-type process following the electron-transfer step. Phenacyl halides react with $(RO)_3P$ or $(RO)_2PO^-$ to yield enol phosphates (Perkow Reaction) by what is formally nucleophilic attack upon the carbonyl oxygen (reaction 5),[21-24] although in some cases

$$PhCOCH_2X + (RO)_3P \rightarrow \underset{\mathbf{1}}{PhC(=CH_2)OP(O)(OR)_2} + RX \quad (5)$$

with $(RO)_3P$ the keto phosphonate is a significant product. However, the keto phosphonate and the enol phosphate are not readily separated.[16]

The photostimulated reaction to form $PhCOCH_2P(O)(OR)_2$ was accompanied by a side-reaction producing $PhCOCH_2CH_2COPh$ (Table II), indicating a reaction of short kinetic chain length. Photolysis of $PhCOCH_2HgCl$ in Me_2SO formed $PhCOCH_2CH_2COPh$ nearly quantitatively in the absence of $(RO)_3P$. Under standard conditions in Me_2SO-d_6, the formation of $PhCOCH_2CH_2COPh$ was monitored by ^1H NMR. With $[PhCOCH_2HgCl]_0$ = 0.1 M, the initial rate of formation of $PhCOCH_2CH_2COPh$ was 2.7×10^{-5} M/s. In the presence of 0.02 M $(t\text{-Bu})_2NO^\bullet$, the appearance of $PhCOCH_2CH_2COPh$ was delayed for 12 min, giving a rate of formation of $PhCOCH_2^\bullet$ of 6×10^{-5} M/s. (This calculation is based on the assumption that $(t\text{-Bu})_2NO^\bullet$ traps only $PhCOCH_2^\bullet$. Photolysis of $PhCOCH_2HgCl$ also produces $^\bullet HgCl$ which may react with a second molecule of $PhCOCH_2HgCl$ to form $PhCOCH_2^\bullet$, $HgCl_2$, and Hg°.[18]) The formation of $PhCOCH_2CH_2COPh$ is obviously not a chain process, and very nearly one molecule of $PhCOCH_2CH_2COPh$ is formed for every two radicals trapped by $(t\text{-Bu})_2NO^\bullet$. With $(PhCOCH_2)_2Hg$, similar experiments demonstrated that 0.9 mol of the mercurial was photochemically decomposed (in the absence of nitroxide) for every two radicals trapped by the nitroxide.

The ratio of $PhCOCH_2CH_2COPh/PhCOCH_2P(O)(OMe)_2$ was quite insensitive to the concentration of $(MeO)_3P$ (entries 2-4, 6, 7 of Table II) at constant

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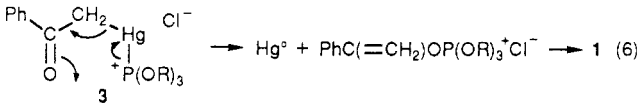
$[PhCOCH_2HgCl]_0$. On the other hand, the ratio increased with the initial concentration of $PhCOCH_2HgCl$. However, a doubling of $[PhCOCH_2HgCl]_0$ caused the ratio to increase (entries 3, 5, 6 of Table II) by only ~1.3 (i.e., $\sim 2^{1/2}$). Such a kinetic behavior is consistent with the steady state concentration of $PhCOCH_2^{\bullet}$ being determined by an initiation process first-order in $PhCOCH_2HgCl$ and a termination reaction second order in $PhCOCH_2^{\bullet}$. However, the data would be consistent with Scheme II only if the steady state $[PhCOCH_2^{\bullet}]$ was proportional to $[PhCOCH_2HgCl]^{1/2}[(MeO)_3P]$. This unusual behavior suggests an initiation reaction where rate is proportional to $[PhCOCH_2HgCl][(MeO)_3P]^2$. This in turn suggests the formation of complexes of the type $PhCOCH_2Hg[P(OMe)_3]^+Cl^-$ and $PhCOCH_2Hg[P(OMe)_3]_2^+Cl^-$ with the latter being the main source of $PhCOCH_2^{\bullet}$ upon photolysis. Further evidence for complexes of this type became evident from a study of the dark (ionic) reactions of $PhCOCH_2HgCl$ with $(RO)_3P$ in Me_2SO.

Ionic Reactions of $PhCOCH_2HgCl$. In the dark $PhCOCH_2HgCl$ reacted slowly with $(MeO)_3P$ in Me_2SO to form the enol phosphate **1** (R = Me) and the enol ether derivative of dimethyl sulfide, **2**. The mercury was mainly

$$PhC(=CH_2)OCH_2SCH_3$$
2

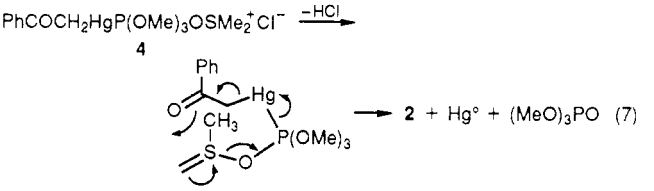
reduced to the Hg° state while significant amounts of $PhCOCH_3$ and $(MeO)_3PO$ were also formed, but no $PhCOCH_2CH_2COPh$ was detected. The enol phosphate **1** was also formed in PhH or DMF in the dark. This Perkow-type product is probably not formed by nucleophilic attack at the carbonyl group because of the unfavorable polarity in $PhCOCH_2^{\delta-}\cdots HgCl^{\delta+}$. Instead, we postulate nucleophilic attack of $(RO)_3P$ at mercury followed by electrophilic attack at the carbonyl oxygen with the electron flow as described in **3** of reaction 6.



Product **2** is reminiscent of the Pummerer reaction observed for sulfoxides.[19] However, sulfoxonium salts such as $PhCOCH_2OSMe_2^+X^-$ are known to undergo elimination to PhCOCHO rather than react via the Pummerer route.[26] $PhCOCH_2HgCl$ in Me_2SO at 80 °C failed to form **2** in the absence of $(MeO)_3P$ while in the presence of $(EtO)_3P$ at 25 °C in Me_2SO, **1** (R = Et) but not **2** was formed. Furthermore, **2** was not formed when other proton acceptors such as Et_3N were substituted for $(MeO)_3P$.

Compound **2** is also formed in the rearrangement of $PhCOCH_2SMe_2^+$ described by Ratts and Yao in a process thought to proceed via $PhCOCH_2S(CH_3)=CH_2$.[27] This suggests that in the presence of $(MeO)_3P$ perhaps Me_2SO is deoxygenated to Me_2S which reacts to form **2**. However, reaction of Me_2S with $PhCOCH_2HgCl$ in Me_2SO failed to form **2** even in the presence of Et_3N as a proton acceptor. Reaction of Me_2S with $PhCOCH_2HgCl$ and $(MeO)_3P$ in DMF also did not form **2** although the enol phosphate **1** was formed. Finally, reaction of Me_2S and $(MeO)_3P$ with $PhCOCH_2HgCl$ in Me_2SO-d_6 formed $PhC(=CH_2)OCD_2SCD_3$ devoid of nondeuterated species under conditions where the recovered Me_2S had not undergone appreciably deuterium exchange.

The formation of **2** from $PhCOCH_2HgCl$ and $(MeO)_3P$ in Me_2SO solution can be rationalized by the formation of a sulfoxonium intermediate **4** from the complex between $(MeO)_3P$ and the mercurial (reaction 7). Indeed the dark



reaction yielding a mixture of **1** and **2** was accompanied by the formation of $(MeO)_3PO$. Acetophenone was also observed, but it is difficult to determine its source since acetophenone was formed in the aqueous thiosulfate workup employed to remove any unreacted mercurial before GC analysis or product isolation. However, the proton lost in converting **4** to the sulfur–ylide presumably leads to the formation of some $PhCOCH_3$ by electrophilic attack upon $PhCOCH_2HgCl$.

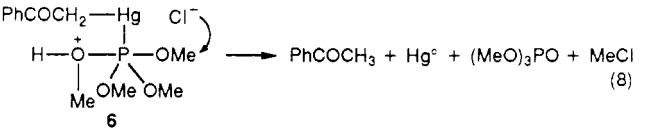
Reactions in Methanol Solution. In MeOH at −50 °C, the photostimulated formation of $PhCOCH_2P(O)(OMe)_2$ from $PhCOCH_2HgCl$ and $(MeO)_3P$ was the major reaction pathway. However, with 5 equiv of $(RO)_3P$ in the dark or upon irradiation at 25 °C in ROH (R = Me or Et), the phosphonate **5** was the major reaction product (24 h

$$PhC(OR)(CH_3)P(O)(OR)_2$$
5a, R = Me; **b**, R = Et

reaction period) accompanied by $(RO)_3PO$ and Hg°. In MeOH with $(EtO)_3P$, only **5a** was detected, indicating that the mercurial had catalyzed a rapid alkoxy exchange in the trialkyl phosphite.

Reaction of $(PhCOCH_2)_2Hg$ with MeOH in the presence of $(MeO)_3P$ rapidly (5 min) formed $PhCOCH_3$. Acetophenone also accompanied **5a** in the reaction of $PhCOCH_2HgCl$, but only traces of $PhC(OMe)_2CH_3$ were detected after 24 h. Acetophenone in $MeOH/(MeO)_3P$ in the presence of $HgCl_2$ or *p*-toluenesulfonic acid initially (5 min) formed $PhC(OMe)_2CH_3$, but with time **5a** was formed; with 10% PTSA after 24 h **5a** was the only product and was formed in essentially quantitative yield.

The methanolysis of (benzoylmethyl)mercurials is strongly catalyzed by trialkyl phosphites in an overall process giving oxidation $[(RO)_3PO]$ and reduction (Hg°) products in the case of $PhCOCH_2HgCl$. One possible mechanism involves association of MeOH with the complex $PhCOCH_2HgP(OR)_3^+Cl^-$. This explains the rapid alkoxy exchange noted. The intermediate **6** could lead to acetophenone (reaction 8), which could react with general acid catalysis to form $PhC(OMe)_2CH_3$, which is slowly but irreversibly converted to **5a**.



Only traces of the enol phosphonate **1** were detected in the reactions of $PhCOCH_2HgCl/MeOH/(MeO)_3P$ or $PhCOCH_3/MeOH/(MeO)_3P/PTSA$. Methanolysis of $PhC(Me)(OSO_2Me)P(O)(OEt)_2$ in the presence of 2,6-lutidine is reported to form $PhC(Me)(OMe)P(O)(OEt)_2$ and **1** in a 5:1 ratio,[28] but in the absence of base, **1** might be methanolyzed to acetophenone and $(MeO)_3PO$.

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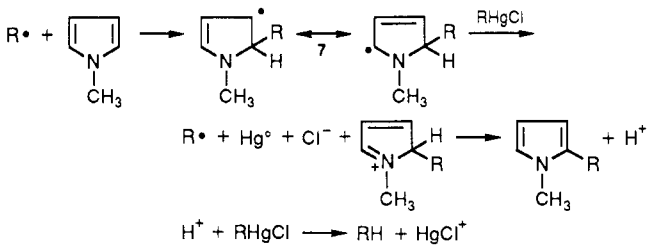
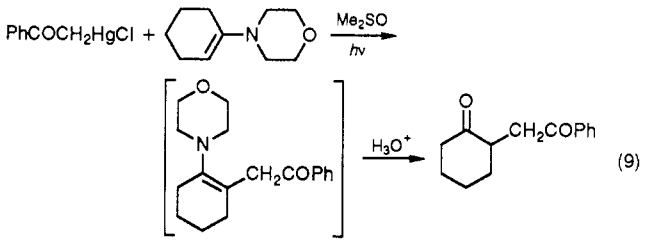
Scheme III. (R = $PhCOCH_2$·)



Reaction of $PhCOCH_2HgCl$ with $(RO)_2PO^-$. An excess of $(RO)_2PO^-$ converts $PhCOCH_2HgCl$ to $PhCOCH_3$ by nucleophilic attack at the mercury atom. Since products such as $PhC(=CH_2)OP(OR)_2$, $PhC(=CH_2)OCH_2SCH_3$, and even $PhCOCH_2P(O)(OR)_2$ could be formulated as arising from further thermal or photochemical reactions of $PhCOCH_2HgP(O)(OR)_2$ (possibly formed from the decomposition of $PhCOCH_2HgP(OR)_3{}^+Cl^-$), we examined the products of a stoichiometric reaction of $PhCOCH_2HgCl$ and $(MeO)_2PO^-$. However, this reaction failed to produce the products observed upon reaction with $(MeO)_3P$. The reaction yielded after workup only acetophenone or upon photolysis a mixture of acetophenone and 1,4-diphenyl-1,4-butanedione. It does not appear that $PhCOCH_2HgP(O)(OMe)_2$ plays a significant role in the reactions involving $(MeO)_3P$.

Reactions of Benzoylmethyl Radicals with Pyrroles and Enamines. *tert*-Butylmercury halides will undergo a free-radical chain reaction with pyridines or pyridinium salts where the *t*-Bu· is trapped by PyH^+ or Py···Hg(R)X.[7,29] With $PhCOCH_2HgCl$ these reactions are inefficient or do not occur at all. Conversely, *t*-BuHgCl fails to react with *N*-methylpyrrole while $PhCOCH_2HgCl$ undergoes a regiospecific free-radical chain substitution process (Scheme III). Again, *t*-Bu· and $PhCOCH_2$· show dramatic differences in their reactivities toward the electron-poor pyridine complexes and the electron-rich pyrrole nucleus. Reaction of $PhCOCH_2HgCl$ with 4 equiv of *N*-methylpyrrole in Me_2SO with fluorescent irradiation for 4 h formed after aqueous $Na_2S_2O_3$ workup, 0.20 equiv of the 2-(benzoylmethol)pyrrole, 0.42 equiv of acetophenone, and 0.07 equiv of $PhCOCH_2CH_2COPh$.

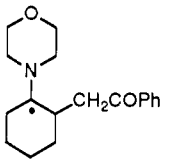
Enamines fail to undergo free-radical substitution reactions with *t*-BuHgCl/$h\nu$ but react readily with $PhCOCH_2HgCl$ upon irradiation (reaction 9). Reaction



(9)

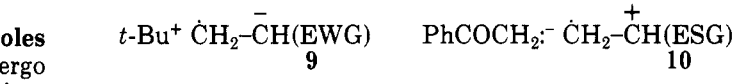
of 1.1 equiv of 4-(1-cyclohexenyl)morpholine with $PhCOCH_2HgCl$ in Me_2SO (10 h, 350-nm irradiation), followed by aqueous $Na_2S_2O_3/CH_2Cl_2$ extraction and heterogeneous hydrolysis of the CH_2Cl_2 extract, yielded 33% of acetophenone and 60% of 2-(benzoylmethyl)cyclohexanone in a very clean reaction that was free of $PhCOCH_2CH_2COPh$. The trimethylsilyl enol ether of cyclohexanone also reacted with $PhCOCH_2HgCl$ upon photolysis to form the diketone after workup. However, the yield was lower (12%) than for the enamine.

The free-radical chain substitution in enamines or pyrroles involves intermediate adduct radicals **7** or **8**.



8

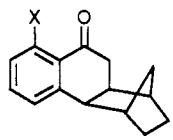
Radicals of the type $R_2N-C(R)_2$· are known to have unusually low oxidation potentials with $E_{1/2}{}^{ox}$ in the range of −1 V (sce).[30] The irreversible half-wave reduction potentials of alkylmercury halides are typically more positive than −0.6 V.[31] There is thus considerable driving force for **7** or **8** to undergo electron transfer to $PhCOCH_2HgCl$. The low reactivity of electron-rich systems such as enamines or pyrroles towards *t*-Bu· is apparently connected with the electron-donating properties of *t*-Bu· where facile addition to electron-poor alkenes occurs because of a polar contribution to the transition state described by **9** (EWG = electron-withdrawing group). Conversely, addition of $PhCOCH_2$· to electron-rich systems such as enamines should occur because of stabilization from structure **10** (ESG = electron-supplying group). Other electrophilic



9 **10**

radicals such as fluorinated alkyl radicals are known to add to enamines to form adduct radicals capable of undergoing electron transfer to a variety of fluorohalocarbons.[32,33] The electrophilic $(EtO_2C)_2CH$· is also reported to react with $CH_2=C(NMe_2)Ph$ or the trimethylsilyl enol ether of cyclohexanone.[34] With a 5- to 10-fold excess of the alkene, the reaction of $(EtO_2C)_2CHBr/Bu_3SnH/h\nu$ gave after hydrolysis $(EtO_2C)_2CHCH_2COPh$ (16%) and 2-(dicarbethoxymethyl)cyclohexanone (59%).[34]

Reactions of (Benzoylmethyl)mercurials with Norbornene. Photolysis (350 nm) of $PhCOCH_2HgCl$ or $(PhCOCH_2)_2Hg$ in Me_2SO or Me_2SO–PhH solvents with an excess of norbornene (typically 5 equiv) leads to the formation of **11a**, $PhCOCH_3$, and small amounts of



11a, X = H
b, X = Br
c, X = I

$PhCOCH_2CH_2COPh$. With $(PhCOCH_2)_2Hg$, as much as 0.66 equiv of **11a** was formed per mole of the mercurial, and the yield of $PhCOCH_3$ after workup was only 0.13 equiv. With $PhCOCH_2HgCl$, **11a** was formed in 42% yield accompanied by 5% of $PhCOCH_3$ and 3% of $PhCOCH_2CHCOPh$. Significant amounts of a dihydro derivative of **11a** were also observed by GCMS. In the presence of DABCO in Me_2SO, the dihydro derivative was

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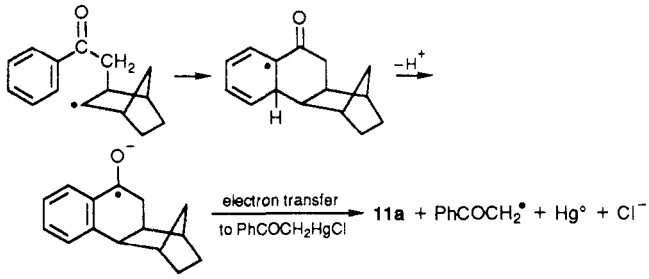
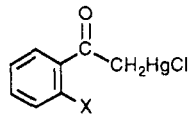
Scheme IV



not observed as a reaction product. Treatment with Jones reagent during workup also removed the dihydro compound.

Addition of $PhCOCH_2^{\bullet}$ to norbornene forms a 3-benzoylpropyl radical, which is known to cyclize under acidic oxidative conditions,[35] and similar cyclizations are known to occur for 3-benzimidoylpropyl radicals [$PhC(=NH)CH_2CH_2C(Me)_2^{\bullet}$] in acidic solution.[36] Scheme IV presents a rationalization for the formation of **11a** in a reaction which is particularly clean in the presence of the base DABCO. The intermediate cyclohexadienyl radical has, of course, a strong driving force to lose a proton and form the aromatic ketyl which would serve as a powerful reducing agent for the (benzoylmethyl)mercurial.

The organomercurials **12b,c** were synthesized in hopes that cyclization of the adduct radicals would occur by halogen atom elimination to form **11a**. However the photolysis of **12b** in the presence of norbornene produced



12a, X = H
b, X = Br
c, X = I

11b in 28% yield and only 8% of **11a** while **12c** yielded **11a** (15%) and a small amount of **11c** whose yield decreased with continued photolysis. Although the process involving cyclization by the elimination of a halogen atom was demonstrated, the regioselectivity of the cyclization step was poor. However, the general method for formation of α-tetralone derivatives from substituted or unsubstituted benzoylmethyl radicals under nonacidic conditions seems quite promising.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were obtained with a Nicolet NT-300 spectrometer in $CDCl_3$ with TMS as the internal standard. Mass spectra were obtained in the GC mode with a Finnigan 4000 with INCOS data system and in the high-resolution mode with a Kratos MS-50 spectrometer. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Analytical gas chromatography was performed with a Varian 3700 chromatograph with a Hewlett-Packard 3390A integrator employing calibration with an internal standard (usually biphenyl) and using 7% OV-3 as the stationary phase. Analytical thin-layer chromatography was performed on glass silica gel plates (Aldrich Chemical Co.) with UV detection. Chromatographic column purifications were performed on 40–140 mesh silica gel (J. T. Baker Co.). The purity of all title compounds was judged to be >95% since significant impurities could not be detected by GC or by ^1H and ^{13}C NMR analyses.

Photostimulated reactions were carried out with solvents deoxygenated by nitrogen bubbling in flasks equipped with rubber septa and with irradiation by a 275-W fluorescent sunlamp (General Electric Co.) ca. 15 cm from the Pyrex reaction vessel or in a 350-nm Rayonet Photoreactor. Both irradiation sources maintained a reaction temperature of 35–40 °C. Dark reactions were performed in flasks wrapped in aluminum foil.

Materials. (2-Oxo-2-phenylethyl)mercury chloride was prepared according to the literature procedure using $HgCl_2$ in place of HgI_2 and had a mp of 145–146 °C.[37] (2-Oxocyclohexyl)mercury chloride, mp 134–135 °C, was made by the same procedure. [2-(o-Bromophenyl)-2-oxoethyl]mercury chloride was prepared by the same method: mp 122–126 °C; ^1H NMR (Me_2SO-d_6) δ 7.66–7.55 (m, 2 H), 7.43 (dt, 1 H, J = 7.5, 1.2 Hz), 7.34 (dt, 1 H, J = 7.5, 1.5 Hz), 3.01 (s, 2 H with ^{199}Hg satellites, J = 330 Hz). [2-(o-Iodophenyl)-2-oxoethyl]mercury chloride recrystallized from CH_2Cl_2–hexane had mp 99–100 °C; ^1H NMR (Me_2SO-d_6) δ 7.86 (d, 1 H, J = 7.5 Hz), 7.58 (d, 1 H, J = 7.5 Hz), 7.44 (t, 1 H, J = 7.5 Hz), 7.15 (t, 1 H, J = 7.5 Hz), 2.99 (s, 2 H with ^{199}Hg satellites, J = 330 Hz). 1-[(Trimethylsilyl)oxy]cyclohexene was prepared from cyclohexanone.[38] All other reagents were obtained from Aldrich Chemical Co.

Dimethyl sulfoxide was distilled over CaH_2 under reduced pressure and stored over activated 4A molecular sieves. Benzene was distilled from sodium and methanol from $Mg(OCH_3)_2$. *N*-Methylpyrrole was distilled over CaH_2 under reduced pressure before use.

Solutions of anions in HMPA were prepared by treatment of the conjugate acid with 1 equiv of Me_3COLi under nitrogen. Similar yields of alkylation products were observed using Me_3COK. After deoxygenation for 15–30 min by nitrogen bubbling, the $PhCOCH_2HgCl$ was added and irradiation commenced. Many of the benzylic carbanions yielded the dimerization products in high yield in the dark, presumably from a thermal electron transfer process.

Isolation Procedures. For the alkylation and oxidative dimerization reactions of Table I, product isolation involved treatment with 50–100 mL of 10% aqueous NaCl or 5% hydrochloric acid followed by Et_2O extraction. For the other alkylation reactions, the reaction mixture was diluted with 50 mL of CH_2Cl_2, a known amount of the GC standard (biphenyl) was added, and the resulting mixture was extracted three times with 15% aqueous $Na_2S_2O_3$ followed by water. The CH_2Cl_2 solution was dried over Na_2SO_4 and analyzed by GLC or evaporated to dryness, and the products were isolated by crystallization or column chromatography.

3-Methyl-1-phenyl-2-buten-1-one.[39] The isolated product had bp 88–90 °C (2 torr): ^1H NMR ($CDCl_3$) δ 8.2–7.8 (m, 2 H), 7.6–7.2 (m, 3 H), 6.72 (m, 1 H), 2.23 (d, 3 H), 2.00 (d, 3 H); IR (neat, cm^{-1}) 1623, 1674; GCMS m/z (rel intensity) 160 (M^+, 97), 159 (100), 145 (75), 105 (90), 77 (97), 51 (59).

3-Nitro-1-phenyl-1-butanone. The product was obtained by chromatography with silica gel using PhH as eluent: ^1H NMR ($CDCl_3$) δ 8.1–7.8 (m, 2 H), 7.6–7.3 (m, 3 H), 4.92 (m, 1 H), 4.05–3.98 (m, 2 H), 1.58 (d, 3 H); IR (KBr pellet, cm^{-1}) 1690, 1450, 1380, 1370; MS m/z (rel intensity) calcd for $C_{10}H_{10}O$ ($M^+ - HNO_2$), 146.07289, found 146.07320 (19), 131 (18), 105 (100), 91 (1.6), 77 (48), 51 (16).

1-Nitro-1,2-diphenylethene. Recrystallization of the crude reaction product in hexane yielded *cis*-α-nitrostilbene as the major product: mp 71–73 °C (yellow needles) [lit.[40] mp 74–75 °C]; ^1H NMR ($CDCl_3$) δ 8.4–7.3; IR (KBr pellet, cm^{-1}) 1550; MS m/z (rel intensity) 225 (M^+, 1), 179 (100), 152 (12), 102 (12), 89 (47), 76 (34), 51 (21), 46 (4).

2,3-Dinitro-2,3-diphenylbutane. The product was obtained as a mixture of diastereomers in a 2.5:1 ratio (^1H NMR) by crystallization of the crude reaction product from methanol–water. The mixture of isomers had mp 120–40 °C; ^1H NMR ($CDCl_3$) δ

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8.10–7.05 (m), 2.32 (s), 2.20 (s); IR (KBr pellet, cm^{-1}) 1550, 1350. Repeated recrystallizations yielded the pure *dl*-isomer: mp 138–140 °C [lit.[41] mp 138–140 °C]; ^1H NMR ($CDCl_3$) δ 8.1–7.1 (m, 10 H), 2.30 (s, 6 H); IR (KBr pellet, cm^{-1}) 1550, 1350; HRMS m/z calcd for $C_{20}H_{16}$ ($M^+ - N_2O_4$) 208.12528, found 208.12492.

Diethyl (Benzoylmethyl)malonate.[42] The product was obtained by silica gel chromatography using PhH (75%)–$CHCl_3$ (25%) as eluent: ^1H NMR ($CDCl_3$) δ 8.1–7.2 (m, 5 H), 4.35–3.95 (m, 5 H), 3.02 (d, 2 H), 1.27 (t, 6 H); IR (neat, cm^{-1}) 1740, 1690; MS m/z (rel intensity) 278 (M^+, 0.5), 233 (3), 187 (8), 173 (2), 105 (100), 77 (26), 55 (4).

Diethyl (Benzoylmethyl)methylmalonate. The product was isolated by chromatography using PhH–$CHCl_3$ as the eluent: ^1H NMR (CCl_4) δ 8.1–7.2 (m, 5 H), 4.2 (q, 4 H), 3.08 (s, 2 H), 1.66 (s, 3 H), 1.28 (t, 6 H); IR (KBr pellet, cm^{-1}) 1735, 1688; MS m/z (rel intensity) calcd for $C_{16}H_{20}O_5$ 292.13110, found 292.13068 (0.2), 247 (2), 173 (23), 105 (100), 77 (36), 51 (5).

Diethyl (Benzoylmethyl)ethylmalonate.[43] The product was isolated by chromatography: ^1H NMR ($CDCl_3$) δ 8.2–7.2 (m, 5 H), 4.18 (q, 4 H), 3.05 (s, 2 H), 2.02 (q, 2 H), 1.28 (t, 6 H), 0.95 (t, 3 H); MS m/z (rel intensity) 306 (M^+, 0.2), 261 (13), 233 (1), 187 (94), 141 (47), 120 (11), 105 (100), 77 (39), 51 (7).

5,5-Dimethyl-1-phenyl-1,4-hexanedione.[44] The isolated material had bp 135–136 °C (2 Torr): ^1H NMR (CCl_4) δ 8.05–7.75 (m, 2 H), 7.55–7.23 (m, 3 H), 3.26–2.64 (m, 4 H), 1.16 (s, 3 H); IR ($CHCl_3$, cm^{-1}) 1680; MS m/z (rel intensity) calcd for $C_{14}H_{18}O_2$ 218.13074, found 218.13022 (7), 105 (100), 77 (49), 51 (29).

1,4-Diphenyl-2-methyl-1,4-butanedione. The product was obtained by column chromatography using PhH (50%)–$CHCl_3$ (50%): mp 101–102 °C; ^1H NMR ($CDCl_3$) δ 8.3–7.3 (m, 10 H), 1.27 (d, 3 H), ABX for $-CHCH_2-$, with δ_A = 3.05, δ_B = 3.76, δ_X = 4.20 (J_{AX} = 5 Hz, J_{BX} = 8 Hz, J_{AB} = 18 Hz); IR (KBr pellet, cm^{-1}) 1599, 1617; HRMS calcd for $C_{17}H_{16}O_2$ 252.11508, found 252.11467.

2,2-Dimethyl-1,4-diphenyl-1,4-butanedione. The product was obtained by chromatography using PhH (50%)–$CHCl_3$ (50%) as eluent: ^1H NMR ($CDCl_3$) δ 8.1–7.2 (m, 10 H), 3.08 (s, 2 H), 1.25 (s, 6 H); IR (KBr pellet, cm^{-1}) 1666, 1364; MS m/z (rel intensity) 266 (M^+, 4), 144 (6), 105 (100), 77 (42), 51 (14).

1,2-Dibenzoyl-1,1,2,2-tetraphenylethane. The product was obtained by recrystallization of the reaction product from PhH–MeOH: mp 146.5–147.5 °C [lit.[45] mp 148–151 °C]; ^1H NMR ($CDCl_3$) δ 8.3–7.1; IR (KBr pellet, cm^{-1}) 1665.

1,4-Diphenyl-1,4-butanedione. A solution of 0.5 mmol of $PhCOCH_2HgCl$ in 5 mL of Me_2SO was photolyzed in a Rayonet Photoreactor for 8 h at ~35 °C to give 78% of 1,4-diphenyl-1,4-butanedione after silica gel chromatography using hexane (80%)–ethyl acetate (20%) as eluent: ^1H NMR ($CDCl_3$) δ 8.04 (d, 4 H, J = 7 Hz), 7.57 (t, 2 H, J = 7 Hz), 7.47 (t, 4 H, J = 7 Hz), 3.46 (s, 4 H); MS m/z (rel intensity) 238 (M^+, 12), 133 (10), 105 (100), 77 (38).

Dimethyl (Benzoylmethyl)phosphonate.[46] Solutions of $PhCOCH_2HgCl$ and $(MeO)_3P$ in Me_2SO (Table II) were photolyzed at 30 °C with a sunlamp for 17 h to give a mixture of $PhCOCH_2P(O)(OMe)_2$, $PhCOCH_2CH_2COPh$, $(MeO)_3PO$, and $PhCOCH_3$ (by GC). Pure $PhCOCH_2P(O)(OMe)_2$ was obtained by chromatography using hexane (40%)–ethyl acetate (60%) as eluent: ^1H NMR ($CDCl_3$) δ 8.00 (d, 2 H, J = 7.8 Hz), 7.60 (t, 1 H, J = 7.2 Hz), 7.48 (t, 2 H, J = 7.5 Hz), 3.78 (d, 6 H, $^3J_{P,H}$ = 11.4 Hz), 3.65 (d, 2 H, $^2J_{P,H}$ = 22.5 Hz); MS m/z (rel intensity) 228 (M^+, 15), 200 (2), 151 (10), 105 (100), 91 (8), 77 (33).

Diethyl (Benzoylmethyl)phosphonate.[46] Irradiation (350 nm) of 0.50 mmol of $PhCOCH_2HgCl$ and 2.5 mmol of $(EtO)_3P$ in 5 mL of Me_2SO for 8 h gave 0.08 mmol of $PhCOCH_2CH_2COPh$ and 0.17 mmol of $PhCOCH_2P(O)(OEt)_2$ having GCMS m/z (rel intensity) 256 (M^+, 5), 211 (3), 146 (13), 120 (17), 105 (100), 77 (28).

Dimethyl 1-Phenylethenyl Phosphate (1, R = Me).[22,47] Reaction of 0.50 mmol of $PhCOCH_2HgCl$ and 2.5 mmol of $(MeO)_3P$ in 5 mL of refluxing PhH for 2 h gave acetophenone (11%) and **1** (68%). No 1,4-diphenyl-1,4-butanedione was detected. Column chromatography on silica gel with ethyl acetate (25%)–hexane (75%) furnished pure **1**: ^1H NMR ($CDCl_3$) δ 7.64–7.56 (m, 2 H), 7.42–7.32 (m, 3 H), 5.32 (t, 1 H, J = 3 Hz), 5.23 (t, 1 H, J = 3 Hz), 3.86 (d, 6 H, $^3J_{P,H}$ = 11.1 Hz). Sunlamp irradiation of $PhCOCH_2HgCl$ and $(MeO)_3P$ (5 equiv) in PhH for 17 h produced $PhCOCH_3$, $PhCOCH_2P(O)(OMe)_2$, and $PhCOCH_2CH_2COPh$ but not **1**.

Dimethyl 1-Cyclohexenyl Phosphate.[22] Reaction of 0.5 mmol of (2-oxocyclohexyl) mercury chloride with 2.5 mmol of $(MeO)_3P$ in 5 mL of Me_2SO for 20 min yielded 95% of the cyclohexanone enol phosphate: ^1H NMR ($CDCl_3$) δ 5.45–5.37 (m, 1 H), 3.73 (d, 6 H, $^3J_{P,H}$ = 11.1 Hz), 2.20–2.07 (m, 2 H), 2.05–1.95 (m, 2 H), 1.70–1.60 (m, 2 H), 1.55–1.40 (m, 2 H); GCMS m/Z (rel intensity) 206 (M^+, 13), 127 (100), 109 (15), 97 (12), 79 (39).

[1-[(Methylthio)methoxy]ethenyl]benzene (2).[27] A mixture of 0.50 mmol of $PhCOCH_2HgCl$ and 2.5 mmol of $(MeO)_3P$ in 5 mL of Me_2SO was stirred in the dark at 25 °C for 48 h to give after workup $PhCOCH_3$ (53%), **1** (13%), and **2** (25%). Pure **2** was obtained by column chromatography using ethyl acetate (4%)–hexane (96%) as eluent: ^1H NMR ($CDCl_3$) δ 7.68–7.60 (m, 2 H), 7.38–7.26 (m, 3 H), 5.02 (s, 2 H), 4.81 (d, 1 H, J = 3 Hz), 4.29 (d, 1 H, J = 3 Hz), 2.27 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.30, 135.98, 128.51, 128.06, 125.34, 84.90, 71.86, 15.01; MS m/z calcd for M^+ 180.06089, found 180.06174.

Dimethyl 1-Methoxy-1-phenylethyl Phosphate (5a). A mixture of 0.5 mmol of $PhCOCH_2HgCl$ and 2.5 mmol of $(MeO)_3P$ in 5 mL of CH_3OH was stirred in the dark for 48 h at 25 °C. Workup gave $PhCOCH_3$ (16%) and **5a** (51%). No 1,4-diphenyl-1,4-butanedione or enol phosphate (**1**) was observed. Pure **5a** was isolated by column chromatography using ethyl acetate (50%)–hexane (50%) as eluent: ^1H NMR ($CDCl_3$) δ 7.52 (d, 2 H, J = 6.9 Hz), 7.39 (t, 2 H, J = 7.2 Hz), 7.32 (t, 1 H, J = 6.9 Hz), 3.68 (d, 3 H, $^3J_{P,H}$ = 10.2 Hz), 3.63 (d, 3 H, $^3J_{P,H}$ = 10.5 Hz), 3.22 (s, 3 H), 1.87 (d, 3 H, $^3J_{P,H}$ = 15.9 Hz); ^{13}C NMR ($CDCl_3$) δ 137.60, 128.07, 127.82, 127.62, 79.19 (d, $J_{P,C}$ = 168 Hz), 53.85 (d, $J_{P,C}$ = 6.5 Hz), 50.19 (d, $J_{P,C}$ = 12.6 Hz), 18.73; MS m/z calcd for M^+ 244.08645, found 244.08667.

***N*-Methyl-2-(benzoylmethyl)pyrrole.** A mixture of 0.50 mmol of $PhCOCH_2HgCl$ and 2.0 mmol of *N*-methylpyrrole in 5 mL of Me_2SO was irradiated at 350 nm for 4 h. Workup yielded $PhCOCH_3$ (42%), $PHCOCH_2CH_2COPh$ (7%), and 20% of the substituted pyrrole. A pure sample of *N*-methyl-2-(benzoylmethyl)pyrrole was obtained by chromatography with ethyl acetate (10%)–hexane (90%) as eluent: ^1H NMR ($CDCl_3$) δ 8.02 (d, 2 H, J = 7.2 Hz), 7.57 (t, 1 H, J = 7.5 Hz), 7.46 (t, 2 H, J = 7.5 Hz), 6.61 (t, 1 H, J = 2.4 Hz), 6.08 (t, 1 H, J = 3 Hz), 6.05–5.95 (m, 1 H), 4.26 (s, 2 H), 3.55 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 196.35, 136.21, 133.22, 128.58, 128.48, 125.27, 122.53, 108.90, 107.03, 37.07, 34.07; MS m/z calcd for M^+ 199.09972, found 199.09904.

Reaction of $PhCOCH_2HgCl$ with *N*-Morpholino-1-cyclohexene To Form 2-(Benzoylmethyl)cyclohexanone. Photolysis (350 nm) of 0.50 mmol of the enamine and 0.55 mmol of $PhCOCH_2HgCl$ in 5 mL of Me_2SO for 10 h yielded metallic mercury. Workup with aqueous $Na_2S_2O_3$ yielded a CH_2Cl_2 solution whose GCMS was consistent with the substitution of $PhCOCH_2$ for the vinyl hydrogen atom: m/z (rel intensity) 285 (M^+, 8), 200 (3), 180 (100), 165 (31), 105 (12), 77 (14). Hydrolysis of the extract with 20 mL of 1 M hydrochloric acid for 30 min yielded 2-(benzoylmethyl)cyclohexanone (60%) and acetophenone (33%). The 2-(benzoylmethyl)cyclohexanone isolated by column chromatography had the following NMR properties: ^1H NMR ($CDCl_3$) δ 7.99 (d, 2 H, J = 7.2 Hz), 7.56 (t, 1 H, J = 7.5 Hz), 7.46 (t, 2 H, J = 7.5 Hz), 3.61 (dd, 1 H, J = 17.7, 6.6 Hz), 3.18 (sextet, 1 H, J = 6.3 Hz), 2.69 (dd, 1 H, J = 17.7, 5.7 Hz), 2.45 (q, 2 H, J = 4.5 Hz), 2.27–2.00 (m, 2 H), 1.95–1.58 (m, 3 H), 1.45 (dq, 1 H, J = 12.6, 3.9 Hz). The same ^1H NMR was observed from the diketone synthesized from the enamine and phenacyl bromide.

Reaction of $PhCOCH_2HgCl$ with the Trimethylsilyl Enol Ether of Cyclohexanone. Photolysis (350 nm) of 0.5 mmol of

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$PhCOCH_2HgCl$ in the presence of 2.5 mmol of the enol ether for 22 h in 5 mL of PhH (90%)–Me_2SO (10%) gave after workup 12% of 2-(benzoylmethyl)cyclohexanone, 13% of $PhCOCH_2CH_2COPh$, and 14% of $PhCOCH_3$.

2,3,4,4a,10,10a-Hexahydro-(1α,4α,4aα,10aα)-1*H*-1,4-methanophenanthren-9-one (11a). A mixture of 0.5 mmol of $PhCOCH_2HgCl$ and 2.5 mmol of norbornene in 5 mL of PhH (90%)–Me_2SO (10%) was irradiated at 350 nm for 16 h. Workup yielded **11a** (42%), $PhCOCH_3$ (5%), and 1,4-diphenyl-1,4-butanedione (3%). Pure **11a** was obtained by column chromatography with ethyl acetate (5%)–hexane (95%) as eluent: ^1H NMR ($CDCl_3$) δ 7.78 (dd, 1 H, *J* = 7.5, 1.2 Hz), 7.50 (dt, 1 H, *J* = 7.5, 1.5 Hz), 7.32 (d, 1 H, *J* = 7.5 Hz), 7.26 (t, 1 H, *J* = 7.5 Hz), 3.05 (d, 1 H, *J* = 8.4 Hz), 2.72 (dd, 1 H, *J* = 15.6, 9.0 Hz), 2.50 (dd, 1 H, *J* = 15.6, 4.2 Hz), 2.40–2.30 (m, 1 H), 2.24 (br s, 1 H), 2.10 (br s, 1 H), 1.74–1.48 (m, 3 H), 1.44–1.34 (m, 1 H), 1.26 (d, 1 H, *J* = 10.8 Hz), 1.01 (d, 1 H, *J* = 10.8 Hz); ^{13}C NMR ($CDCl_3$) δ 199.97, 145.43, 133.75, 133.27, 129.12, 125.79, 125.06, 46.89, 45.58, 44.79, 42.04, 39.44, 32.60, 30.00, 29.50; MS *m/z* calcd for M^+ 212.12012, found 212.12049.

Reaction of *o*-$BrC_6H_4COCH_2HgCl$ with Norbornene: Formation of 11a,b. Photolysis (350 nm) of 0.50 mmol of *o*-$BrC_6H_4COCH_2HgCl$ with 5 mmol of norbornene in 5 mL of Me_2SO for 17 h yielded 8% of **11a** and 28% of **11b**. The *o*-bromotetralone derivative **11b** had a GCMS, *m/z* (rel intensity) 292 (M^+, 36), 290 (M^+, 37), 225 (60), 224 (88), 223 (73), 222 (78), 143 (26), 128 (21), 115 (100).

Reaction of *o*-$IC_6H_4COCH_2HgCl$ with Norbornene: Formation of 11a,c. Photolysis of 0.50 mmol of the mercurial and 5.0 mmol of norbornene in 5 mL of Me_2SO at 350 nm for 22 h yielded after workup 15% of **11a** and a small amount of **11c**: GCMS *m/z* (rel intensity) 338 (M^+, 100), 271 (67), 270 (96), 144 (20), 128 (19), 127 (7), 115 (73).

Registry No. 1 (R = Me), 4202-12-4; **2**, 14439-02-2; **5a**, 124316-33-2; **11a**, 124375-87-7; **11b**, 124286-47-1; **11c**, 124286-48-2; $PhCOCH_2HgCl$, 28531-58-0; Me_2CHNO_2, 79-46-9; $MeCH_2NO_2$, 79-24-3; H_3CNO_2, 75-52-5; $PhCH_2NO_2$, 622-42-4; $PhCH(Me)NO_2$, 7214-61-1; $EtCH(CO_2Et)_2$, 133-13-1; $MeCH(CO_2Et)_2$, 609-08-5; $H_2C(CO_2Et)_2$, 105-53-3; $PhCH(CO_2Et)_2$, 83-13-6; Me_3COCH_3, 75-97-8; $PhCOCHMe_2$, 611-70-1; $PhCOCH_2Me$, 93-55-0; $PhCOCH_2Ph$, 451-40-1; $PhCOCHPh_2$, 1733-63-7; $Ph_2CHC{\equiv}N$, 86-29-3; $PhCOCH_2CMe_2NO_2$, 124286-37-9; $PhCOCH{=}Me_2$, 5650-07-7; $PhCOCH_2CHMeNO_2$, 7404-78-6; $PhCOCH{=}C(Me)NO_2$, 124286-38-0; $PhCO(CH_2)_2NO_2$, 62847-52-3; $O_2NCH_2H_8Cl$, 124286-39-1; $PhCOCH_2CH(Ph)NO_2$, 124286-40-4; $PhCH{=}C(Ph)NO_2$, 1215-07-2; $PhCH(NO_2)CH(NO_2)Ph$, 67765-80-4; (*S*,*S*)-$PhC(Me)(NO_2)C(Me)(NO_2)Ph$, 124286-41-5; (*R*,*S*)-$PhC(Me)(NO_2)C(Me)(NO_2)Ph$, 22486-14-2; $PhCOCH_2C(Et)(CO_2Et)_2$, 124286-42-6; $PhCOCH_2C(Me)(CO_2Et)_2$, 124286-43-7; $PhCOCH_2CH(CO_2Et)_2$, 94011-49-1; $PhCOCH_2CH(Ph)(CO_2Et)_2$, 124286-44-8; $PhC(CO_2Et)_2C(CO_2Et)_2Ph$, 117720-83-9; $PhCO(CH_2)_2COCMe_3$, 56079-45-9; $PhCOCH_2CMe_2COPh$, 124286-45-9; $PhCOCH_2CH(Me)COPh$, 15982-59-9; $PhCOCH(Ph)CH_2COPh$, 4441-01-4; $PhCOCH(Ph)CH(Ph)COPh$, 10516-92-4; $PhCOC(Ph)_2C(Ph)_2COPh$, 113680-01-6; $Ph_2C(CN)C(CN)Ph_2$, 3122-21-2; $(MeO)_3P$, 121-45-9; $PhCOCH_2P(O)(OMe)_2$, 1015-28-7; $(PhCOCH_2)_2Hg$, 37160-45-5; $PhCOCH_2P(O)(OEt)_2$, 3453-00-7; $(EtO)_3P$, 122-52-1; $Ph\text{-}CO(CH_2)_2COPh$, 495-71-6; *o*-$BrC_6H_4COCH_2HgCl$, 124286-49-3; *o*-$IC_6H_4COCH_2HgCl$, 124286-50-6; dimethyl 1-cyclohexenyl phosphate, 3719-53-7; (2-oxocyclohexyl)mercury chloride, 14839-64-6; *N*-methyl-2-(benzolmethyl)pyrrole, 124286-46-0; *N*-methylpyrrole, 96-54-8; *N*-morpholino-1-cyclohexene, 670-80-4; 2-(benzoylmethyl)cyclohexanone, 33553-23-0; cyclohexanone trimethylsilyl enol ether, 6651-36-1; norbornene, 498-66-8.

Supplementary Material Available: NMR spectra of $PhCOCH_2P(O)(OMe)_2$ (^1H), $PhC(OMe)(Me)P(O)(OMe)_2$ (^1H, ^{13}C), $PhC(=CH_2)OP(O)(OMe)_2$ (^1H), $PhC(=CH_2)OCH_2SCH_3$ (^1H, ^{13}C), N-methyl-2-(benzoylmethyl)pyrrole (^1H, ^{13}C), and **11a** (^1H, ^{13}C) (17 pages). Ordering information is given on any current masthead page.

Stereochemistry of the Intermolecular and Intramolecular Conjugate Additions of Amines and Anions to Chiral (*E*)- and (*Z*)-Vinyl Sulfoxides. Total Syntheses of (*R*)-(+)-Carnegine and (+)- and (−)-Sedamine[1]

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The intramolecular addition of incipient amine anions to chiral (*E*)- and (*Z*)-vinyl sulfoxides occurs in the same diastereofacial sense, giving chiral isoquinoline and piperidine derivatives that differ in relative stereochemistry at C-2. In contrast, the conjugate addition reactions of (*E*)- and (*Z*)-β-styryl *p*-tolyl sulfoxide with benzylamine and $LiCH(CO_2Et)_2$ are diastereoconvergent processes. The same major diastereomeric product is obtained in each case. We have attempted to rationalize the stereochemical outcome of the addition of nucleophiles to chiral vinyl sulfoxides according to the type of nucleophilic reagent employed (either chelating/hydrogen bonding or nonchelating) and from a consideration of possible transition states.

The addition of nucleophiles to chiral vinyl sulfoxides has proven to be a useful method for the asymmetric synthesis of chiral molecules and natural products.[2,3] A detailed understanding of the steric and electronic factors that control the stereochemical course of these reactions, however, remains unclear. Recent theoretical calculations

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