Three-Component Radical Condensations Involving Benzoylmethyl Radicals, Alkenes, and Diphenyl Disulfide

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Acyl-substituted methyl radicals ($RCOCH_2^•$; R = H, Me, Ph), generated by photolysis of $RCOCH_2HgCl$, add to alkenes, enol ethers, or vinyl sulfides to give adduct radicals that are readily trapped by PhSSPh to yield a three-component condensation product. The presence of an alkali metal carbonate is crucial in preventing side reactions resulting in the conversion of the mercurial to $RCOCH_3$ by PhSH formed in the photolysis.

Introduction

Radical processes are becoming increasingly important in syntheses.[1] Formation of carbon–carbon bonds by the addition of a radical to an alkene requires an efficient product formation step to avoid losses from telomerization or radical–radical interactions. Some of the methods developed and utilized in chain reactions are atom transfers of the Kharasch-type;[2] the use of R_3SnH, $CH_2{=}CHCH_2SnR_3$,[4] $ROC(S)SSnR_3$,[5a] silyl hydrides,[6] thiohydroxamic esters,[7] and other thiocarbonyl compounds,[5b,c] RHgH,[1a] R_3B,[8] or RHgX,[9] to trap adduct radicals; electron transfer to or from adduct radicals;[10,11] or β-elimination of adduct radicals to yield substitutive alkylation products.[12] In nonchain processes adduct radicals can be trapped reductively by SmI_2 or Cr(II)[13,14] or oxidatively by Mn(III).[15] However, the majority of these methods are suitable mainly for the trapping of the adducts of nucleophilic radicals with external electron-deficient alkenes although many examples of Kharasch-type additions involving electrophilic radicals are known and Mn(III) cyclizations of the adduct radicals obtained from malonate, acetoacetic ester, and related electrophilic radicals represents an important synthetic method.[15] The addition of nitro- or carbonyl-conjugated radicals to enamines followed by electron transfer from the adduct radical to $PhCOCH_2HgCl$, $Me_2C(NO_2)_2$, or $p\text{-}O_2NC_6H_4CH_2Cl$ also occurs readily.[11b,c]

We describe herein a method of forming carbon–carbon bonds by intermolecular addition of carbonyl-substituted radicals to electron-rich alkenes by use of PhSSPh to trap the adduct radical. Photolysis of R^1COCH_2HgCl (R^1 = H, Me, Ph) produces the electrophilic enolyl radical which readily adds to electron-rich alkenes because of a favorable polar effect.[16] We have reported that in the absence of trapping agents the photostimulated reaction of $PhCOCH_2HgCl$ with norbornene produces a cyclized α-tetralone.[11b] This reaction proceeds via an intermediate cyclohexadienyl radical formed by annelation of the adduct radical and the aromatic ring of the benzoyl group. The reaction also occurs readily for alkenes such as 1-hexene, reaction 1.

$$PhCOCH_2HgCl + R^2CH{=}CHR^3 \xrightarrow[Me_2SO]{h\nu} \text{1} + PhCOCH_2CH(R^2)CH_2R^3 \quad \text{2} \qquad (1)$$

1		2
46%	a, R^2 = H; R^3 = Bu	5%
21%	b, $R^2 = R^3 = -(CH_2)_4-$	19%

We thought that if a suitable trapping agent could be found which would selectively trap the nucleophilic adduct radical but not the electrophilic benzoylmethyl radical, the three-component condensation reaction 2 should occur.

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Scheme I

$$R^1COCH_2HgCl \xrightarrow{h\nu} R^1COCH_2^\bullet + HgCl^\bullet$$

$$R^1COCH_2^\bullet + R^2CH{=}CHR^3 \longrightarrow \underset{\mathbf{3}}{R^1COCH_2CH(R^2)CH(R^3)^\bullet}$$

$$\mathbf{3} + RSSR \longrightarrow \underset{\mathbf{4}}{R^1COCH_2CH(R^2)CH(R^3)SR} + RS^\bullet$$

$$RS^\bullet + HgCl^\bullet \longrightarrow PhSHgCl$$

Table I. Photostimulated Reaction of $PhCOCH_2HgCl$ with $c\text{-}C_6H_{10}$ with RSSR[a]

RSSR (equiv)	solvent	Li_2CO_3 (mmol)	conditions	% yield[b] $PhCOCH_3$	5	6[c]
Ph(2)	Me_2SO	0	dark, 24 h	95[d]	0	0
Ph(2)	Me_2SO	0	$h\nu$, 6 h	53	tr	27
Ph(2)	Me_2SO	1	$h\nu$, 6 h	34	2	46
Ph(4)	Me_2SO	1	$h\nu$, 6 h	25	4	63
Ph(4)	DMF	1	$h\nu$, 6 h	34	3	43
Bu(2)	Me_2SO	1	$h\nu$, 6 h	30		34[e]
Ph(2)	Me_2SO	1	$h\nu$, 6 h[f]	54	11	7
Ph(1)[g]	Me_2SO	1	$h\nu$, 6 h		2	46
Ph(5)[g]	Me_2SO	1	$h\nu$, 6 h		11	43
Ph(10)[g]	Me_2SO	1	$h\nu$, 6 h		15	30
Ph(20)[g]	Me_2SO	1	$h\nu$, 6 h		17	17

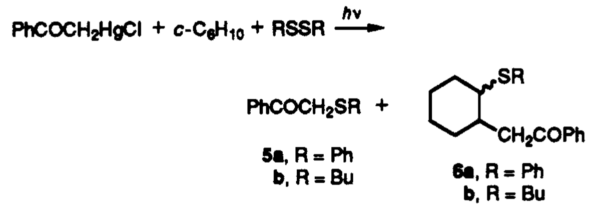
[a] Reaction of 0.25 mmol of the mercurial with 1–2.5 mmol of $c\text{-}C_6H_{10}$ in 5 mL of solvent irradiated in a 350-mm Rayonet photoreactor at 40 °C. [b] GC yield with an internal standard after workup with aqueous $Na_2S_2O_3$. [c] A mixture of *cis* and *trans* diastereomers, ~1:1. [d] $PhCOCH_3$ results from the workup of $PhCOCH_2HgCl$ with aqueous $Na_2S_2O_3$. All $PhCOCH_2HgCl$ was destroyed upon 6 h of photolysis. [e] Also formed, 5% of **1b** and 11% of **2b**. [f] Reaction employed $(PhCOCH_2)_2Hg$. [g] 0.5 mmol of $PhCOCH_2HgCl$ and 2.5 mmol of $c\text{-}C_6H_{10}$.

The present report describes the successful utilization of PhSSPh as such a trapping agent.

$$PhCOCH_2HgCl + R^2CH{=}CHR^3 + X{-}Z \rightarrow PhCOCH_2CH(R^2)CH(R^3)X + Z\,HgCl \quad (2)$$

Results and Discussion

Cyclohexene. The chain transfer constant of polystyrenyl radical (a nucleophilic radical) with PhSSPh is about 17 times greater than that for poly(methyl methacrylate) radical (an electrophilic radical).[17] [The relative values of k_p for styrene and methyl methacrylate are in the ratio of 1:5]. We thus decided to investigate disulfides as trapping agents for the adduct radicals formed by the addition of $PhCOCH_2^\bullet$ to alkenes, Scheme I. Since the phenylthiyl radical has been shown to displace an alkyl radical (e.g., *tert*-butyl) from an alkylmercurial,[18] the possibility exists that Scheme I could involve a chain mechanism. Scheme I involves four paramagnetic species. For the reaction to succeed, $R^1COCH_2^\bullet$ should react faster with the alkene than with RSSR while radical **3** should react faster with RSSR. To test the feasibility of this process, the photostimulated reaction of $PhCOCH_2HgCl$, RSSR, and cyclohexene was investigated, reaction 3 and Table I.



(3)

The last four entries of Table I allow the relative reactivities of cyclohexene and PhSSPh toward $PhCOCH_2^\bullet$ to be calculated as 4.6, 3.9, 4.0, and 4.0, respectively.

One notable feature of the data of Table I is the complete absence of products formed by the addition of $PhS^\bullet$ to cyclohexene ($PhSC_6H_{11}$ or $PhSC_6H_{10}SPh$). It is known that the addition of thiyl radicals to alkenes is reversible and k_{-1}/k_2[RSSR] has been determined to be relatively large, reaction 4.[19] The addition of $PhS^\bullet$ to alkenes is

$$RS^\bullet + R^2CH{=}CHR^3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RSCH(R^2)CHR^{3\bullet} \xrightarrow{k_2[RSSR]} RSCH(R^2)CH(R^3)SR + RS^\bullet \quad (4)$$

more reversible than the corresponding reactions involving alkylthiyl radicals such as $t\text{-}BuS^\bullet$ because of the ~10 kcal/mol resonance stabilization of $PhS^\bullet$.[20] Another notable feature of the results is the complete absence of the cyclization product **1b** when PhSSPh was used as the trapping agent. The rate constant for the homolytic bimolecular displacement of $PhS^\bullet$ from PhSSPh is known to be in the order of 10^6 M^{-1} s^{-1}.[21,22] This restricts the rate constant for the cyclization of **3** (R^1 = Ph) derived from cyclohexene to $<10^3$ s^{-1}. With the less reactive BuSSBu,[22] some cyclization was detected (Table I).

One unexpected feature of the data of Table I is the dramatic effect of Li_2CO_3 which increases the yield of **6** and decreases the yield of $PhCOCH_3$. Another surprising result was the observation that $(PhCOCH_2)_2Hg$ was much less effective than $PhCOCH_2HgCl$ in forming **6** and in the presence of Li_2CO_3 the ratios of $PhCOCH_3$/**6** were much higher upon the photolysis of $(PhCOCH_2)_2Hg$ than of $PhCOCH_2HgCl$. Only traces of $PhCOCH_2CH_2COPh$ were observed from either mercurial under the conditions of Table I. In the absence of the alkene/PhSSPh, $PhCOCH_2CH_2COPh$ was a major product from either of the mercurials. These observations will be explained in a later section concerning the effect of carbonate bases upon the reaction.

Reactions of 1-Alkenes. The degree of substitution at a double bond plays an important role in determining the rate of addition of an alkyl radical to an alkene. For example, the methyl radical adds 6.5 times more readily to 1-butene than to *cis*-2-butene at 65 °C.[23] Therefore, it was expected that the $R^1COCH_2^\bullet$ radical would show an even greater selectivity in reactions with 1-alkenes than with cyclohexene. In Table II are summarized the results of photochemical reactions of a 4-fold excess of 1-alkenes with R^1COCH_2HgCl, PhSSPh, and Li_2CO_3 (in a 1:2:5 mol ratio) in Me_2SO. As expected the 1-alkenes gave better yields of the trapping products **4** (R^2 = H) than did cyclohexene. The substituted alkenes, $CH_2{=}CH$-

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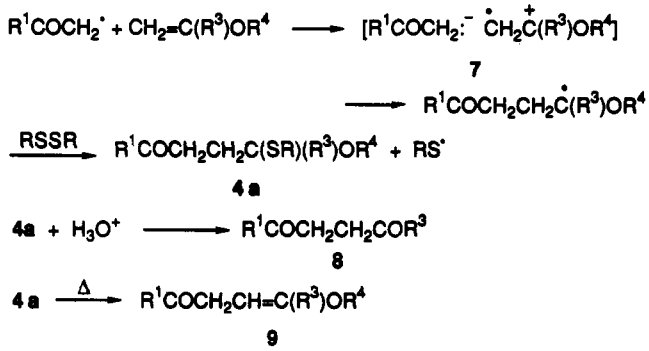
(23) Marcoux, L. S.; Adams, R. N.; Feldberg, S. W. *J. Phys. Chem.* **1969**, *73*, 2611.

Table II. Photochemical Reactions of R^1COCH_2HgCl with CH_2=CHR^3 and PhSSPh To Yield 4 (R^2 = H)[a]

R^1	R^3 in CH_2=CHR^3 (mmol)	% 4 (R = Ph, R^2 = H)[b]
Ph	Bu (0.30)	67
Ph	Bu (1.25)	80
CH_3	Bu (1.25)	92
H	Bu (1.25)	90
Ph	Bu (1.25)	22[c]
Ph	n-C_8H_{17} (0.30)	68
Ph	CH_2OH (1.25)	26
Ph	CH_2OAc (1.25)	34
Ph	CH_2OSiMe_3 (1.25)	84
Ph	$SiMe_3$ (0.30)	66
Ph	$SiMe_3$ (1.25)	90
CH_3	$SiMe_3$ (1.25)	90
H	$SiMe_3$ (1.25)	86

[a] Reaction of 0.25 mmol of R^1COCH_2HgCl, 0.50 mmol of PhSSPh, and 1.25 mmol of Li_2CO_3 in 2.5 mL of Me_2SO in a 350-mm Rayonet photochemical reactor at 40 °C for 6 h. [b] GC yield with an internal standard after aqueous $Na_2S_2O_3$ workup. [c] With BuSSBu. Also formed 31% of **1a**.

Scheme II



CH_2OSiMe_3 or CH_2=$CHSiMe_3$, gave excellent yields of the three-component condensation products. However, the more easily polymerized CH_2=CHPh failed to give significant amounts of 4 (R^2 = H, R^3 = Ph) with PhSSPh. With BuSSBu the cyclized α-tetralone (**1a**) was the major product with 1-hexene while t-BuSSBu-t failed to give any of the trapped product 4 (R = t-Bu, R^2 = H, R^3 = Bu).

Reactions of Enol Ethers. The electrophilic carbonyl-substituted methyl radical is expected to react faster with more electron-rich alkenes such as enol ethers because of stabilization of the transition state structure **7**, Scheme II. The trapped product **4a** is an *O,S*-acetal which can be readily hydrolyzed to the 1,4-dione **8**. The *O,S*-acetals were often unstable to GC analysis, e.g., R^1 = R^3 = R^4 = Ph, and eliminated PhSH to form **9**. The acetals **4a** with R^4 = Ph were much more resistant to hydrolysis than the acetals with R^4 = Et or Bu while the *O,S*-acetals from 1-ethoxy- or 1-(trimethylsiloxy)cyclohexene underwent hydrolysis upon workup with aqueous $Na_2S_2O_3$ in the absence of any added acid to form **10**. On the other hand, the *O,S*-thioacetals from dihydropyran were stable to the workup conditions and compounds **11** could be isolated, predominantly or exclusively as the cis isomers. Table III summarizes the results.

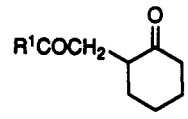
The ^1H NMR spectra of **11c** and **11d** showed a single cis-substituted diastereomer with an axial–equatorial coupling of the methine hydrogens of 3.9–4.2 Hz.[24] With **11a** or **11b** the cis isomers predominated over the trans by a factor of 5.5–6. Giese has demonstrated that the reaction of tetraacetylglucosyl bromide with Bu_3SnH in the presence of CH_2=CHCN affords the coupling product with

(24) Giese, B.; Dupuis, J. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 896.

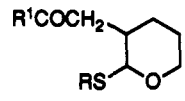
Table III. Photochemical Reactions of R^1COCH_2HgCl with Enol Ethers in the Presence of PhSSPh and Li_2CO_3[a]

R^1	enol ether	product (%)[b]
Ph	CH_2=CHOEt	$PhCOCH_2CH_2CHO$ (55)[c]
Ph	CH_2=CHOBu	$PhCOCH_2CH_2CHO$ (56)[c]
Ph	CH_2=CHOPh	$PhCOCH_2CH_2(SPh)OPh$ (37)[d]
Ph	1-ethoxycyclohexene	**10c** (58)
CH_3	1-ethoxycyclohexene	**10b** (35)
H	1-ethoxycyclohexene	**10a** (37)
Ph	1-(trimethylsiloxy)-cyclohexene[e]	**10c** (40)
Ph	1-(trimethylsiloxy)-cyclohexene	**10c** (51)
CH_3	1-(trimethylsiloxy)-cyclohexene	**10b** (40)
Ph	dihydropyran	*cis*-**11c** (43)[d]
Ph	dihydropyran	*cis*-**11d** (43)[f]
CH_3	dihydropyran	**11b** (32)[g]
H	dihydropyran	**11a** (42)[h]
Ph	CH_2=CHOBu	$PhSO_2CH_2CH(OBu)SPh$ (40)[i]

[a,b] See Table II. [c] After hydrolysis with 2 M hydrochloric acid. [d] Eliminated PhSH under GC conditions. Yield measured for elimination product. [e] 0.30 mmol. [f] BuSSBu instead of PhSSPh. [g] cis/trans = 6. [h] cis/trans = 5.5. [i] $PhSSO_2Ph$ instead of PhSSPh. Yield based on $PhSSO_2Ph$.

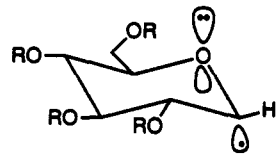


10, **a**, R^1 = H
b, R^1 = CH_3
c, R^1 = Ph

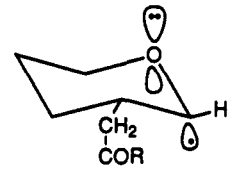


11, **a**, R^1 = H, R = Ph
b, R^1 = CH_3, R = Ph
c, R^1 = R = Ph
d, R^1 = Ph, R = Bu

an axial substituent at C-1 with a stereoselectivity decreasing from a/e = 50 to 3.5 when the ring substituents are changed from OAc to OMe.[25] The stereoselectivity was ascribed to a preferred structure for the intermediate σ-radical (**12**). A similar explanation explains the high preference for the formation of the axial trapping product (i.e., syn addition) from the adduct radical **13** with the equatorial preference of the substituent CH_2COR decreasing from R = Ph to R = H or Me.



12



13

Toward alkyl radicals $PhSSO_2Ph$ has a reactivity approximately the same as PhSSPh. However, when $PhSSO_2Ph$ was substituted for PhSSPh under the conditions of Table III, the only significant product formed from CH_2=CHOBu was $PhSO_2CH_2CH(OBu)SPh$. This product reflects the higher reactivity and lower reversibility relative to PhS· for the attack of $PhSO_2$· upon the alkene. With PhSeSePh the addition product analogous to **4a** was not observed, presumably because the very reactive PhSeSePh trapped $PhCOCH_2$· before addition to the vinyl ether could occur.[18]

Reaction of Vinyl Sulfides. The reactions of $PhCOCH_2HgCl$ with vinyl sulfides in the presence of

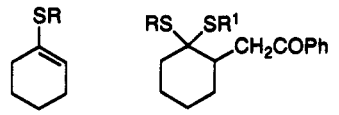
(25) Dupuis, J.; Giese, B.; Ruegge, D. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 896.

Table IV. Photochemical Reactions of $PhCOCH_2HgCl$ with 14 in the Presence of PhSSPh or BuSSBu[a]

vinyl sulfide	R in RSSR	products (%)[b]
14a	Ph	15a (30),[c] 17a (3),[d] 6a (4)[e]
14a	Bu	17a (23),[d] 6a (26)[e]
14b	Ph	15b (51)[c,e]
14b	Bu	17b (23), 6b (34)[e]

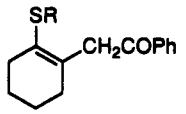
[a] See Table II. [b] GC yield unless otherwise noted. [c] Isolated yield. [d] GC yield of the dione 10c after hydrolysis with $HgCl_2$ in MeCN (75%)–H_2O (25%). [e] Mixture of cis and trans isomers. [f] In the absence of RSSR or Li_2CO_3.

disulfides were expected to yield thioacetals or upon hydrolysis the 1,4-diones. However, phenyl vinyl sulfide gave only traces of $PhCOCH_2CH_2CH(SPh)_2$ and polymerization appeared to be the major reaction pathway. Reactions of the less easily polymerized 1-cyclohexenyl sulfides 14 with $PhCOCH_2HgCl$ and PhSSPh yielded the expected thioacetals 15a,b which readily lost PhSH under GC conditions to form the vinyl sulfides 16. The saturated

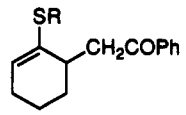


14, a, R = Ph
b, R = Bu

15, a, R = R¹ = Ph
b, R = Ph, R¹ = Bu
c, R = R¹ = Bu

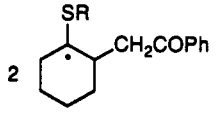


16, a, R = Ph
b, R = Bu



17, a, R = Ph
b, R = Bu

sulfides 6 and unsaturated sulfides 17 were also initial reaction products formed in low yields with PhSSPh as the trapping agent but as the predominant products with BuSSBu or in the absence of any disulfide. The adduct radicals 18 must disproportionate to 6 and 17. In the absence of a disulfide none of the isomeric 16 was observed, indicating high regiochemical control for the disproportionation, reaction 5. Again, a much higher reactivity was



18, a, R = Ph
b, R = Bu

observed for PhSSPh than for BuSSBu in the trapping of the adduct radical 18 and 15c could not be detected.[22] Although 15b was formed from the reaction of PhSSPh with 18b, reaction of 18a with BuSSBu did not occur and only disproportionation products 6b and 17b were observed. Table IV summarizes pertinent results.

Evidence against a Free Radical Chain Mechanism. Attempts to initiate a chain reaction by use of AIBN at 80 °C were unsuccessful. Although PhS• readily displaces *t*-Bu• from *t*-BuHgCl leading to a variety of free radical chain reactions such as *t*-BuHgCl + PhSSPh → *t*-BuSPh + PhSHgCl or PhCH=CHSPh + *t*-BuHgCl → *t*-BuCH=CHPh + PhSHgCl,[18] the displacement of $PhCOCH_2$• from $PhCOCH_2HgCl$ by PhS• probably does not occur readily. Furthermore, the photolysis of $PhCOCH_2HgCl$ under the conditions employed in Tables I–IV occurs rapidly giving a high radical flux that would not be conducive to a chain reaction.

Measurement of kinetic chain length using the *t*-Bu_2NO• (DBNO) inhibition method is not easily applied to photochemically initiated processes in the presence of PhSSPh. We thus applied this technique to an allylic substitution process involving the formation of PhS• by a β-elimination, reaction 6.[12f,26] The initial rate of for-

$$PhCOCH_2HgCl + CH_2{=}CHCH_2SPh \xrightarrow{h\nu} \underset{\textbf{19 (70\%)}}{PhCOCH_2CH_2CH{=}CH_2} + \underset{4\%}{PhSSPh} + \underset{9\%}{PhCOCH_3} \quad (6)$$

mation of 19 with 0.1 M $PhCOCH_2HgCl$ under the standard photochemical conditions of Tables I–IV was 6.4×10^{-4} M min^{-1} (by ^1H NMR). Under similar conditions in the presence of 1.25×10^{-2} M DBNO, compound 19 could not be detected until after 20 min of photolysis. This leads to a photochemical rate of formation of radicals trapped by DBNO of 6×10^{-4} M min^{-1}. A possible scenario is that only $PhCOCH_2$• is trapped by DBNO and that only 1 mol of 19 is produced per mol of $PhCOCH_2$• generated photochemically. It must be concluded that under the conditions employed the reaction PhS• + $PhCOCH_2HgCl$ → $PhCOCH_2$• + PhSHgCl plays little or no role and that both reaction 6 and the general process of Scheme I are photochemical reactions with quantum yields <1. The formation of $PhCOCH_2$• in Scheme I is thus formulated as involving direct photolysis of the mercurial and not via photodissociation of PhSSPh followed by displacement of $PhCOCH_2HgCl$ from the mercurial. Thus, the rate of disappearance of $PhCOCH_2HgCl$ upon photolysis was about the same in the presence or absence of PhSSPh or a mixture of PhSSPh and CH_2=CHSiMe$_3$. Photochemical electron transfer between $PhCOCH_2HgCl$ and PhSSPh does not appear to be important.

Role of Alkali Carbonates. Table V presents additional evidence demonstrating the importance of alkali carbonates in the formation of γ-(phenylthio) carbonyl compounds from alkenes.

Organomercurials of the type $RCOCH_2HgCl$ are known to readily react with proton donors to form $RCOCH_3$.[27] For example, mixing 1 equiv of HCl, ammonium salts, or PhSH with $PhCOCH_2HgCl$ in Me_2SO-d_6 forms $PhCOCH_3$ rapidly and quantitatively (by ^1H NMR). Thus, it appears that alkali carbonates prevent the cleavage of the mercurial by neutralization of acidic byproducts formed in the photochemical reaction. In the dark the reaction of $PhCOCH_2HgCl$, PhSSPh, and c-C_6H_{10} in Me_2SO-d_6 failed to form significant amounts of $PhCOCH_3$ by ^1H NMR. The photochemical formation of PhS• and its reaction with allylic hydrogen atoms to form PhSH[28] seems a likely route to a reagent capable of destroying $PhCOCH_2HgCl$ in an electrophilic manner. When 2 equiv of PhSSPh and 5 equiv of c-C_6H_{10} were photolyzed for 6 h in Me_2SO-d_6 under the standard conditions, a broad ^1H NMR peak at δ 5.35 was observed for PhSH. When 1 equiv of

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Table V. Effects of Bases on the Photochemical Reactions of $PhCOCH_2HgCl$ with Alkenes in the Presence of PhSSPh[a]

alkene	base (mmol)	$PhCOCH_3$ (%)[b]	other (%)[b]
dihydropyran	none	78	*cis*-10c (4)
dihydropyran	DTB (0.50)[c]	70	*cis*-10c (3)
dihydropyran	Na_2CO_3 (1.25)	7	*cis*-10c (33)
dihydropyran	Li_2CO_3 (1.25)	7	*cis*-10c (43)
1-hexene	none	36	$PhCOCH_2CH_2CH(SPh)Bu$ (47)
1-hexene	DABCO (0.50)[d]	76	$PhCOCH_2CH_2CH(SPh)Bu$ (7)
1-hexene	Na_2CO_3 (1.25)	tr	$PhCOCH_2CH_2CH(SPh)Bu$ (72)
1-hexene	Li_2CO_3 (1.25)	tr	$PhCOCH_2CH_2CH(SPh)Bu$ (80)

[a] Reaction of 0.25 mmol of $PhCOCH_2HgCl$, 0.50 mmol of PhSSPh, and 1.25 mmol of alkene in 2.5 mL of Me_2SO in a 350-nm Rayonet photoreactor at 40 °C for 6 h. Workup with aqueous $Na_2S_2O_3$. [b] GC yield with an internal standard. [c] 2,6-Di-*tert*-butylpyridine. [d] 1,4-Diaza[2.2.2]bicyclooctane.

$PhCOCH_2HgCl$ was added after photolysis, the peak at δ 5.35 disappeared and nearly all of the mercurial was converted to $PhCOCH_3$. When the PhSH was first reacted with an excess of Li_2CO_3 before the addition of $PhCOCH_2HgCl$, essentially no $PhCOCH_3$ was formed although some symmetrization of the organomercurial to form $(PhCOCH_2)_2Hg$ was observed. However, the effect of Li_2CO_3 on the reactions of $PhCOCH_2HgCl$ with PhSSPh and alkenes is a bit more subtle than simply converting PhSH to PhSLi. Thus, the photochemical reaction between $PhCOCH_2HgCl$, 1-hexene (5 equiv), PhSSPh (2 equiv), and PhSLi (1 equiv) in Me_2SO failed to form any of the expected $PhCOCH_2CH_2CH(SPh)Bu$ and instead yielded only $PhCOCH_3$ (57%). Since the photolysis had been conducted for 6 h, all of the $PhCOCH_2HgCl$ should have been destroyed before the aqueous $Na_2S_2O_3$ workup. Neither the dimer $PhCOCH_2CH_2COPh$ nor $PhCOCH_2SPh$ was observed although the dimer is formed in high yield when $PhCOCH_2HgCl$ or $(PhCOCH_2)_2Hg$ are photolyzed in the absence of a substrate to trap $PhCOCH_2^{\bullet}$.[11b] Apparently PhSLi is itself an excellent trapping agent for $PhCOCH_2^{\bullet}$ reducing the enolyl radical to the anion. Photolysis of a 1:1 mixture of $PhCOCH_2HgCl$ and PhSLi in Me_2SO-d_6 for 2 h again gave only $PhCOCH_3$ with no $PhCOCH_2CH_2COPh$ or $PhCOCH_2SPh$ and with some symmetrization of the mercurial. However, when 1 equiv of $HgCl_2$ was added at the start of the photolysis, $PhCOCH_2CH_2COPh$ was the major product, $PhCOCH_3$ was not detected, and the mercurial was not symmetrized. It is known that $HgCl_2$ reacts readily with PhSH or PhS^- to form $Hg(SPh)_2$.[29] It thus appears that the dramatic effect of alkali carbonates (Tables I and V) upon the reaction involves not only the conversion of PhSH to PhSLi but also the rapid conversion of PhSLi to $(PhS)_2Hg$ via PhSHgCl. Apparently either $HgCl_2$ or PhSHgCl reacts more rapidly with PhSLi than $PhCOCH_2HgCl$ itself. PhSHgCl can be formed in the photolysis reaction by either the coupling of $PhS^{\bullet}$ and $HgCl^{\bullet}$ or by attack of $HgCl^{\bullet}$ upon PhSSPh. The latter process was demonstrated by the photolysis of a 1:1 mixture ClHgHgCl and PhSSPh in Me_2SO-d_6. In 4 h 63% of the PhSSPh was consumed to form a mixture of PhSHgCl, $(PhS)_2Hg$, and $HgCl_2$.

From the foregoing analysis, it would be expected that substitution of $(PhCOCH_2)_2Hg$ for $PhCOCH_2HgCl$ would result in lower yields of **6a** even in the presence of Li_2CO_3, confirming the experimental result (Table I). Although the Li_2CO_3 would still neutralize the PhSH, in the absence of a mercury(II) chloride salt to react with PhSLi, the thiolate anion would reduce $PhCOCH_2^{\bullet}$ to $PhCOCH_2^-$ and prevent the formation of significant amount of **6a**.

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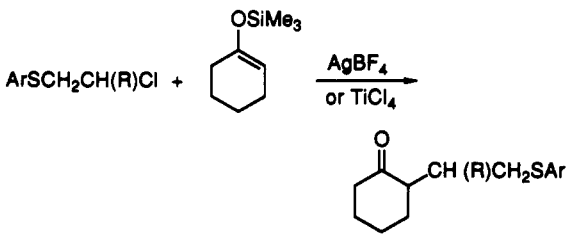
Conclusions

The reactions of carbonyl-substituted methyl radicals with electron-rich alkenes in the presence of PhSSPh and a base such as Li_2CO_3 represents a convenient method for the regioselective formation of new carbon–carbon bonds. The use of $CHOCH_2HgCl$ to extend a carbon chain and the use of enol ethers or vinyl sulfides to form 1,4-dicarbonyl compounds are interesting features of these reactions.

The preparation of γ-(arylthio) carbonyl compounds under ionic conditions has been previously reported in the reactions of episulfonium ions with siloxyalkenes, e.g., reaction 7.[30] However, in these processes the enol derivative mainly attacks the more substituted carbon atom of the episulfonium ion to yield products that are regioisomers to those produced in reaction 2 with X–Z = PhSSPh. Conversion of terminal alkenes to $ArSCH_2CH(R)Cl$ with ArSCl followed by reaction with siloxyalkenes gives a low regioselectivity, except in the case of styrene, in contrast to the high regioselectivity demonstrated in the free radical processes summarized in Tables II and III.



(7)

Experimental Section

General Methods. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were obtained with a Nicolet NT 300 spectrometer 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. Analytical gas chromatography was performed with a Varian 3700 chromatograph equipped with a Hewlett-Packard 3390A integrator 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. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Most products were isolated by either flash column chromatography on silica gel (Kiesel gel, 230–400-mesh ASTM, purchased from EM Reagents Co.) or by preparative TLC. GC yields were determined using biphenyl as an internal standard and are corrected with predetermined response factors.

Materials. Dimethyl sulfoxide was distilled from CaH_2 and stored over 4-Å molecular sieves under nitrogen atmosphere. DMF was distilled from CaH_2. (Benzoylmethyl)mercury chloride

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($PhCOCH_2HgCl$) and bis(benzoylmethyl)mercury [$(PhCOCH_2)_2Hg$] were prepared as described previously.[11b] (Acetylmethyl)mercury chloride was prepared by reaction of isopropenyl acetate and mercuric acetate followed by treatment with KCl,[31] mp 103–104 °C (lit.[31] mp 103–104 °C): ^1H NMR (Me_2SO-d_6) δ 2.06 (s, 3 H), 2.56 (s, 2 H with ^{199}Hg satellites, J = 324 Hz). (Formylmethyl)mercury chloride [$HC(=O)CH_2HgCl$] was prepared by reaction of vinyl acetate and mercuric acetate followed by treatment with aqueous KCl,[31] mp 129–130 °C dec (lit.[31] mp 129–130 °C): ^1H NMR (Me_2SO-d_6) δ 2.61 (d, J = 5.1 Hz, 2 H with ^{199}Hg satellites, J = 325 Hz), 9.32 (t, J = 5.1 Hz, 1 H). 1-[(Trimethylsilyl)oxy]cyclohexene was prepared from cyclohexanone.[32] Phenyl vinyl ether was prepared by a two-step process from ethylene dibromide and phenol:[33] ^1H NMR ($CDCl_3$) δ 4.41 (d, J = 6.0 Hz, 1 H), 4.75 (d, J = 13.8 Hz, 1 H), 6.63 (dd, J = 6.6, 13.8 Hz, 1 H), 6.99 (d, J = 7.8 Hz, 2 H), 7.06 (t, J = 7.5 Hz, 1 H), 7.30 (t, J = 7.8 Hz, 2 H). 1-Ethoxycyclohexene was prepared from cyclohexanone using ethyl orthoformate with a catalytic amount of PTSA:[34] ^1H NMR ($CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3 H), 1.47–1.57 (m, 2 H), 1.61–1.70 (m, 2 H), 2.00–2.08 (m, 4 H), 3.68 (q, J = 7.2 Hz, 2 H), 4.59 (t, J = 3.0 Hz, 1 H). 1-(Butylthio)cyclohexene was prepared from cyclohexanone and BuSH in presence of a catalytic amount of PTSA by dehydration:[35] ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 7.2 Hz, 3 H), 1.41 (apparent sextet, J = 7.5 Hz, 2 H), 1.52–1.73 (m, 2 H), 2.06–2.15 (m, 2 H), 2.65 (t, J = 7.5 Hz, 2 H), 5.61 (br s, 1 H). 1-(Phenylthio)cyclohexene was prepared from cyclohexanone and thiophenol by dehydration with P_2O_5;[35] the ^1H NMR was identical with that in the literature.[36] Phenyl allyl sulfide was prepared from PhSH and allyl bromide with sodium ethoxide in ethanol.[37] $PhSO_2SPh$ was prepared by oxidation of diphenyl disulfide with 30% H_2O_2 in acetic acid.[38] All other reagents were commercially available.

General Procedure for the Photostimulated Reaction of R^1COCH_2HgCl (R^1 = Ph, CH_3, H) with Alkenes in the Presence of Disulfide and Li_2CO_3. The mercurial, disulfide, Li_2CO_3, and a magnetic stir bar were placed in a dry Pyrex test tube and Me_2SO was added by syringe through a rubber septum. The mixture was then deoxygenated by bubbling dry nitrogen through it for about 20 min. After addition of previously deoxygenated alkene via a syringe through the septum, the reaction mixture was irradiated with stirring in a 350-mm Rayonet photoreactor at 40 °C for 6 h.

Isolation Procedure. The reaction mixtures were diluted with 50 mL of CH_2Cl_2, a known amount of biphenyl was added, and the resulting mixture was washed three times with 15% aqueous $Na_2S_2O_3$, followed by water. The CH_2Cl_2 layer was then dried over anhydrous Na_2SO_4 and analyzed by GC or the solvent was removed and products were isolated by column chromatography or preparative TLC. Hexane (98%)/ethyl acetate (2%) was used as eluant for flash column chromatography unless otherwise mentioned.

4-Butyl-1-tetralone (1a). This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 6.9 Hz, 3 H), 1.30–1.50 (br s, 4 H), 1.64–1.75 (m, 2 H), 1.99–2.13 (m, 1 H), 2.17–2.32 (m, 1 H), 2.51–2.63 (m, 1 H), 2.70–2.85 (m, 1 H), 2.86–2.97 (m, 1 H), 7.25–7.33 (m, 2 H), 7.48 (t, J = 7.2 Hz, 1 H), 8.02 (d, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 198.33, 148.53, 133.27, 131.79, 128.19, 127.22, 126.45, 37.94, 34.84, 34.34, 29.79, 26.63, 22.75, 14.01; GCMS m/z (relative intensity) 202 (M^+, 29), 160 (8), 145 (100), 131 (13), 117 (36), 91 (13), 77 (7); HRMS m/z 202.1360 (calcd for $C_{14}H_{18}O$ 202.1358).

1-Phenyl-1-octanone (2a).[39] This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.2 Hz, 3 H), 1.10–1.50 (m, 10 H), 1.65–1.80 (m, 2 H), 2.96 (t, J = 7.2 Hz, 2 H), 7.46 (t, J = 7.2 Hz, 2 H), 7.55 (t, J = 7.2 Hz, 1 H), 7.96 (d, J = 7.5 Hz, 2 H); GCMS m/z (relative intensity) 205 (M^+, 6), 133 (8), 120 (81), 105 (100), 77 (50).

4b,5,6,7,8,8a-Hexahydro-10-phenanthrenone (1b). This material isolated by column chromatography was an 83:17 mixture (by capillary and column GC) of trans and cis ring junctures. The ^1H NMR ($CDCl_3$) was very complex but the following signals were assigned to the major isomer: δ 1.43–2.00 (m, 8 H), 2.31–2.72 (m, 2 H), 2.81–2.99 (m, 2 H), 7.29 (t, J = 7.2 Hz, 2 H), 7.49 (t, J = 7.2 Hz, 1 H), 8.02 (d, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 199.06, 148.58, 133.62, 131.49, 128.35, 127.01, 126.39, 40.48, 39.76, 33.66, 30.03, 29.95, 25.22, 20.79; GCMS (major isomer) m/z (relative intensity) 200 (M^+, 83), 185 (8), 158 (100), 144 (26), 131 (33), 115 (42), 105 (12), 77 (18); HMRS m/z calcd for $C_{14}H_{16}O$ 200.1201 (found 200.1202); GCMS (minor isomer) m/z (relative intensity) 200 (M^+, 100), 185 (44), 158 (81), 131 (59), 115 (45), 105 (39), 91 (20), 77 (29).

(Benzoylmethyl)cyclohexane (2b).[40] This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.95–1.08 (m, 2 H), 1.12–1.33 (m, 2 H), 1.60–1.79 (m, 4 H), 1.90–2.05 (m, 1 H), 2.82 (d, J = 6.6 Hz, 2 H), 7.45 (t, J = 7.2 Hz, 2 H), 7.55 (t, J = 7.2 Hz, 1 H), 7.95 (d, J = 7.2 Hz, 2 H); GCMS m/z (relative intensity) 202 (M^+, 8) 120 (100), 105 (66), 77 (41).

α-(Phenylthio)acetophenone (5a).[41] This compound was isolated as a solid: mp 53–54 °C; ^1H NMR ($CDCl_3$) δ 4.15 (s, 2 H), 7.20–7.70 (m, 5 H), 7.80–8.10 (m, 5 H); GCMS m/z (relative intensity) 230 (M^+, 37), 123 (9), 105 (100), 91 (5), 77 (58). The ^1H NMR was identical to that given in the literature.[41]

1-(Benzoylmethyl)-2-(phenylthio)cyclohexane (6a). This compound was isolated by column chromatography as a mixture of cis and trans isomers in approximately a 1:1 ratio (by ^1H NMR): ^1H NMR ($CDCl_3$, mixture of two isomers) δ 1.05–1.31 (m, 2 H), 1.34–1.38 (m, 6 H), 1.62–1.98 (m, 7 H), 2.05–2.20 (m, 2 H), 2.50–2.63 (m, 1 H), 2.74–2.99 (m, 3 H), 3.36 (dd, J = 6.3, 17.1 Hz, 1 H), 3.64 (br s, 1 H), 3.80 (dd, J = 3.0, 16.0 Hz, 1 H), 7.04–7.58 (m, 16 H), 7.89 (d, J = 7.2 Hz, 2 H), 7.96 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, mixture of two isomers) δ 199.75, 199.63, 137.24, 136.08, 134.82, 132.81, 132.30, 131.22, 128.80, 128.48, 128.40, 128.10, 128.00, 126.86, 126.33, 52.80, 51.74, 43.95, 41.78, 38.91, 36.74, 34.63, 33.18, 31.29, 28.70, 26.58, 25.39, 24.71, 21.97; GCMS m/z (relative intensity) 310 (M^+, 3), 201 (1.5), 190 (68), 105 (100), 77 (45); HRMS m/z 310.1390 (calcd for $C_{20}H_{22}OS$ 310.1391). Anal. Calcd for $C_{20}H_{22}OS$: C, 77.37; H, 7.14; S, 10.33. Found: C, 77.65; H, 7.27; S, 10.19.

1-(Benzoylmethyl)-2-(butylthio)cyclohexane (6b). This compound was identified only by GCMS: major isomer, m/z (relative intensity) 290 (M^+, 2), 201 (1), 170 (100), 114 (38), 105 (65), 78 (30).

1-Phenyl-4-(phenylthio)-1-octanone (4, R = R^1 = Ph, R^2 = H, R^3 = Bu). This compound was isolated as a viscous liquid: ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.2 Hz, 3 H), 1.31 (sextet, J = 7.2 Hz, 2 H), 1.41–1.69 (m, 4 H), 1.82–1.97 (m, 1 H), 2.07–2.21 (m, 1 H), 3.10–3.31 (m, 3 H), 7.19 (t, J = 7.2 Hz, 1 H), 7.26 (t, J = 7.2 Hz, 2 H), 7.38 (d, J = 7.2 Hz, 2 H), 7.44 (t, J = 7.2 Hz, 2 H), 7.55 (t, J = 7.2 Hz, 1 H), 7.93 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 199.88, 136.89, 135.14, 132.97, 131.90, 128.84, 128.53, 128.02, 126.72, 48.43, 35.69, 34.75, 29.13, 28.78, 22.58, 14.14; GCMS m/z (relative intensity) 312 (M^+, 8), 203 (24), 192 (18), 150 (61), 105 (100), 77 (41); HRMS m/z 312.1544 (calcd for $C_{20}H_{24}OS$ 312.1548). Anal. Calcd for $C_{20}H_{24}OS$: C, 76.87; H, 7.74; S, 10.26. Found: C, 76.066; H, 7.89; S, 9.97.

1-Phenyl-4-(phenylthio)-1-dodecanone (4, R = R^1 = Ph, R^2 = H, R^3 = n-C_8H_{17}). This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3 H), 1.26 (br s, 10 H), 1.44–1.56 (m, 2 H), 1.57–1.68 (m, 2 H), 1.82–1.98 (m, 1 H), 2.08–2.22 (m, 1 H), 3.10–3.30 (m, 3 H), 7.19 (t, J = 7.2 Hz, 1 H), 7.26 (t, J = 7.2 Hz, 2 H), 7.39 (d, J = 7.2 Hz, 2 H), 7.44 (t, J = 7.2 Hz, 2 H), 7.55 (t, J = 7.2 Hz, 1 H), 7.94 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 199.81, 136.86, 135.14, 132.93, 131.87, 128.81, 128.49, 127.99, 12.68, 48.82, 35.66, 35.03, 31.85, 29.47, 29.25, 28.76, 26.92,

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22.65, 14.12; GCMS m/z (relative intensity) 368 (M^+, 6), 281 (5), 259 (29), 248 (11), 207 (22), 150 (55), 138 (25), 105 (100), 77 (30); HRMS m/z 368.2170 (calcd for $C_{24}H_{32}OS$ 368.2174).

5-(Phenylthio)-2-nonanone (4, R = Bu, R^1 = Me, R^2 = H, R^3 = Bu). This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.2 Hz, 3 H), 1.29 (sextet, J = 7.2 Hz, 2 H), 1.38–1.62 (m, 4 H), 1.78–1.83 (m, 1 H), 1.87–2.03 (m, 1 H), 2.10 (s, 3 H), 2.61–2.71 (m, 2 H), 3.02–3.20 (m, 1 H), 7.21 (t, J = 7.2 Hz, 1 H), 7.27 (t, J = 7.2 Hz, 2 H), 7.36 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 208.37; 135.11, 131.88, 128.81, 126.72, 48.55, 40.57, 34.62, 30.00, 29.02, 28.18, 22.52, 13.98; GCMS m/z (relative intensity) 250 (M^+, 7), 192 (4), 150 (17), 141 (23), 123 (19), 110 (24), 97 (3), 83 (17), 43 (100); HRMS m/z 250.1386 (calcd for $C_{15}H_{22}OS$ 250.1391). Anal. Calcd for $C_{15}H_{22}OS$: C, 71.95; H, 8.86; S, 12.81. Found: C, 71.90; H, 8.35; S, 13.21.

4-(Phenylthio)octanal (4, R = Ph, R^1 = R^2 = H, R^3 = Bu). This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.2 Hz, 3 H), 1.30 (sextet, J = 7.2 Hz, 2 H), 1.38–1.65 (m, 4 H), 1.71–1.86 (m, 1 H), 1.90–2.04 (m, 1 H), 2.67 (t, J = 7.2 Hz, 2 H), 3.09 (apparent pentet, J = 6.6 Hz, 1 H), 7.22 (t, J = 6.9 Hz), 7.28 (t, J = 7.2 Hz, 2 H), 7.37 (d, J = 7.5 Hz, 2 H), 9.75 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 201.78, 134.79, 132.05, 128.90, 128.86, 48.57, 41.04, 34.42, 29.03, 26.59, 22.52, 13.98; GCMS m/z (relative intensity) 236 (M^+, 11), 192 (3), 179 (3), 150 (9), 127 (20), 110 (100), 109 (61), 67 (34); HRMS m/z 236.1236 (calcd for $C_{14}H_{20}OS$ 236.1235). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.13; H, 8.53; S, 13.57. Found: C, 71.16; H, 8.74; S, 13.68.

1-Phenyl-4-(butylthio)-1-octanone (4, R = R^3 = Bu, R^1 = Ph, R^2 = H). This compound was identified by GCMS only: GCMS m/z (relative intensity) 292 (M^+, 7), 235 (2), 203 (3), 172 (15), 159 (8), 145 (4), 130 (35), 115 (100), 105 (63).

5-Hydroxy-1-phenyl-4-(phenylthio)-1-pentanone (4, R = R^1 = Ph, R^2 = H, R^3 = CH_2OH). This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 1.90–2.04 (m, 1 H), 2.17 (d of pentets, J = 4.8, 7.2 Hz, 1 H), 2.46 (br s, 1 H), 3.16–3.37 (m, 3 H), 3.56–3.69 (m, 2 H), 7.20–7.32 (m, 3 H), 7.39–7.49 (m, 4 H), 7.56 (t, J = 7.2 Hz, 1 H), 7.96 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 199.66, 136.66, 133.16, 132.62, 129.06, 128.90, 128.58, 128.03, 127.50, 63.97, 51.76, 35.50, 25.15; HRMS m/z 286.1022 (calcd for $C_{17}H_{18}OS$ 286.1027).

5-Acetoxy-1-phenyl-4-(phenylthio)-1-pentanone (4, R = R^1 = Ph, R^2 = H, R^3 = CH_2OAc). This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 1.78–1.95 (m, 1 H), 2.01 (s, 3 H), 2.21–2.35 (m, 1 H), 3.17–3.48 (m, 3 H), 4.11 (dd, J = 7.8, 11.1 Hz, 1 H), 4.28 (dd, J = 5.4, 11.1 Hz, 1 H), 7.20–7.32 (m, 3 H), 7.40–7.50 (m, 4 H), 7.57 (t, J = 7.2 Hz, 1 H), 7.97 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 199.17, 170.76, 136.70, 133.56, 133.11, 132.18, 129.03, 128.57, 127.96, 127.36, 66.61, 46.86, 35.55, 25.64, 20.78; HRMS m/z 328.1130 (calcd for $C_{19}H_{20}O_3$ 328.1133).

1-Phenyl-4-(phenylthio)-5-[(trimethylsilyl)oxy]-1-pentanone (4, R = R^1 = Ph, R^2 = H, R^3 = CH_2OSiMe_3). This compound was hydrolyzed to the corresponding alcohol (4, R^3 = CH_2OH) during column chromatography: GCMS m/z (relative intensity) 358 (M^+, 0.2), 343 (1), 268 (11), 249 (2), 233 (5), 159 (100), 145 (19), 129 (30), 105 (51), 77 (24), 73 (48).

1-Phenyl-4-(phenylthio)-5-(trimethylsilyl)-1-pentanone (4, R = R^1 = Ph, R^2 = H, R^3 = CH_2SiMe_3). This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 0.94 (dd, J = 8.4, 15.0 Hz, 1 H), 1.04 (dd, J = 6.6, 15.0 Hz, 1 H), 1.80–1.94 (m, 1 H), 2.03–2.16 (m, 1 H), 3.06 (ddd, J = 5.4, 9.0, 17.1 Hz, 1 H), 3.25 (ddd, J = 6.3, 9.0, 17.1 Hz, 1 H), 3.37–3.47 (m, 1 H), 7.15 (t, J = 7.2 Hz, 1 H), 7.22 (t, J = 7.2 Hz, 2 H), 7.33 (d, J = 7.2 Hz, 2 H), 7.39 (t, J = 7.2 Hz, 2 H), 7.50 (t, J = 7.2 Hz, 1 H), 7.88 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 199.81, 136.89, 135.41, 132.91, 131.73, 128.84, 128.49, 128.00, 126.69, 45.46, 35.23, 31.17, 23.57, –0.69; GCMS m/z (relative intensity) 342 (M^+, 0.5), 327 (0.2), 233 (40), 167 (4), 105 (6), 77 (8), 73 (100); HRMS m/z 342.1466 (calcd for $C_{20}H_{26}OSSi$ 342.1474).

1-Phenyl-4-(phenylthio)-4-(trimethylsilyl)-1-butanone (4, R = R^1 = Ph, R^2 = H, R^3 = $SiMe_3$). This compound was isolated as an off-white solid, mp 60–61 °C: ^1H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 1.85–2.01 (m, 1 H), 2.22–2.36 (m, 1 H), 2.63 (dd, J = 4.2, 9.0 Hz, 1 H), 3.07 (ddd, J = 5.4, 9.0, 17.1 Hz, 1 H), 3.20 (ddd, J = 6.3, 9.0, 17.1 Hz, 1 H), 7.08 (t, J = 7.2 Hz, 1 H), 7.19 (t, J = 7.2 Hz, 2 H), 7.31–7.42 (m, 4 H), 7.51 (t, J = 7.2 Hz, 1 H), 7.80 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 200.05, 138.13, 136.77, 132.83, 129.43, 128.81, 128.42, 127.92, 125.82, 37.04, 34.17, 26.27, –2.30; GCMS m/z (relative intensity) 328 (M^+, 1), 313 (4), 219 (55), 208 (13), 203 (17), 105 (20), 77 (16), 73 (100); HRMS m/z 328.1321 (calcd for $C_{19}H_{24}OSSi$ 328.1317). Anal. Calcd for $C_{19}H_{24}OSSi$: C, 69.46; H, 7.36; S, 9.76; Si, 8.55. Found: C, 69.55; H, 7.27, S, 8.23; Si, 8.32.

5-(Phenylthio)-5-(trimethylsilyl)-2-pentanone (4, R = Ph, R^1 = Me, R^2 = H, R^3 = $SiMe_3$). This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 1.64–1.81 (m, 1 H), 1.95 (s, 3 H), 2.04–2.15 (m, 1 H), 2.46–2.60 (m, 2 H), 2.62–2.75 (m, 1 H), 7.15 (t, J = 7.2 Hz, 1 H), 7.25 (t, J = 7.5 Hz, 2 H), 7.33 (d, J = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 208.62, 138.18, 129.32, 128.82, 125.82, 41.67, 33.66, 29.86, 25.50, –2.38; GCMS m/z (relative intensity) 266 (M^+, 2), 167 (3), 151 (5), 141 (13), 137 (11), 136 (100), 116 (19), 73 (49); HMRS m/z 266.1158 (calcd for $C_{14}H_{22}OSSi$ 266.1161).

4-(Phenylthio)-4-(trimethylsilyl)butanal (4, R = Ph, R^1 = R^2 = H, R^3 = $SiMe_3$). This compound was isolated as a liquid: ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 1.75–1.88 (m, 1 H), 2.06–2.20 (m, 1 H), 2.53 (dd, J = 4.2, 8.4 Hz, 1 H), 2.55–2.73 (m, 2 H), 7.16 (t, J = 7.2 Hz, 1 H), 7.26 (t, J = 7.2 Hz, 2 H), 7.32 (d, J = 7.2 Hz, 2 H), 9.66 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 202.12, 137.63, 129.45, 128.87; 126.01, 42.39, 33.76, 23.93, –2.35; HRMS m/z 252.1003 (calcd for $C_{13}H_{20}OSSi$ 252.1004).

1-Phenyl-1,4-butanedione (8, R^1 = Ph, R^3 = H) (Table II).[42] The reaction mixture was first washed three times with 15% aqueous $Na_2S_2O_3$ and then three times with aqueous 2 M HCl, followed by water. After drying the organic layer and evaporation of the solvent, the product was isolated by flash column chromatography using a 95:5 mixture of hexane and ethyl acetate as eluant: ^1H NMR ($CDCl_3$) δ 2.93 (t, J = 6.3 Hz, 2 H), 3.33 (t, J = 6.3 Hz, 2 H), 7.47 (t, J = 7.2 Hz, 2 H), 7.58 (t, J = 7.2 Hz, 1 H), 7.99 (d, J = 7.2 Hz, 2 H), 9.90 (s, 1 H); GCMS m/z (relative intensity) 162 (M^+, 0), 134 (38), 120 (20), 105 (100), 77 (66); CIMS (NH_3) = 163 (MH^+). The ^1H NMR compared favorably with that in the literature.[42]

1-Phenyl-4-(phenylthio)-4-phenoxy-1-butanone (4a, R = R^1 = R^4 = Ph, R^3 = H). This compound was isolated as a solid, mp 69–71 °C: ^1H NMR ($CDCl_3$) δ 2.38 (q, J = 6.9 Hz, 1 H), 2.39 (q, J = 6.9 Hz, 1 H), 3.23 (t, J = 6.9 Hz, 1 H), 3.24 (t, J = 6.9 Hz, 1 H), 5.61 (t, J = 6.6 Hz, 1 H), 6.95–7.03 (m, 3 H), 7.22–7.31 (m, 5 H), 7.39–7.47 (m, 4 H), 7.54 (t, J = 7.2 Hz, 1 H), 7.93 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 199.00, 156.62, 136.68, 134.39, 133.09, 131.26, 129.41, 128.79, 128.54, 128.13, 127.94, 121.99, 116.89, 84.59, 34.69, 30.22; CIMS (NH_3, solids probe) m/z (relative intensity) 366 (M + NH_4^+, 15), 255 (M^+ – OPh, 100), 239 (M^+ – SPh, 12).

2-(Benzoylmethyl)cyclohexanone (10c).[43] This compound was isolated by flash column chromatography using a 95:5 ratio of hexane and ethyl acetate as a solid, mp 42–44 °C: ^1H NMR ($CDCl_3$) δ 1.45 (dq, J = 3.9, 12.6 Hz, 1 H), 1.58–1.95 (m, 3 H), 2.00–2.27 (m, 2 H), 2.45 (q, J = 4.5 Hz, 2 H), 2.69 (dd, J = 5.7, 17.7 Hz, 1 H), 3.18 (sextet, J = 6.3 Hz, 1 H), 3.61 (dd, J = 6.6, 17.7 Hz, 1 H), 7.46 (t, J = 7.5 Hz, 2 H), 7.56 (t, J = 7.5 Hz, 1 H), 7.99 (d, J = 7.2 Hz, 2 H). The same ^1H NMR was observed for the diketone synthesized by reaction of phenacyl bromide and *N*-morpholino-1-cyclohexene: GCMS m/z (relative intensity) 216 (M^+, 12), 159 (3), 120 (43), 105 (100), 97 (17), 77 (42).

2-(Acetylmethyl)cyclohexanone (10b).[44] This compound was isolated as a liquid using hexane (95%)–ethyl acetate (5%) as the eluant in flash column chromatography: ^1H NMR ($CDCl_3$) δ 1.18–1.44 (m, 1 H), 1.53–1.92 (m, 3 H), 2.01–2.18 (m, 3 H), 2.20 (s, 3 H), 2.29–2.43 (m, 2 H), 2.89–3.03 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 211.40, 207.26, 46.39, 43.14, 41.80, 33.94, 30.43, 27.83, 25.24; GCMS m/z (relative intensity) 154 (M^+, 17), 139 (2), 121 (3), 111 (23), 97 (33), 83 (12), 55 (40), 43 (100); HRMS m/z 154.0998 (calcd for $C_9H_{14}O_2$ 154.0994).

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2-(Formylmethyl)cyclohexanone (10a).[45] This compound was isolated as a liquid using hexane (95%)–ethyl acetate (5%) as eluant in flash column chromatography: ^{1}H NMR ($CDCl_3$) δ 1.43 (dq, J = 3.6, 12.6 Hz, 1 H), 1.59–1.83 (m, 2 H), 1.84–1.96 (m, 1 H), 2.00–2.50 (m, 5 H), 2.90–3.03 (m, 2 H), 9.81 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 210.69, 200.68, 45.43, 43.58, 41.71, 33.99, 27.70, 25.20; HRMS m/z 140.0837 (calcd for $C_8H_{12}O_2$ 140.0837).

***cis*-3-(Benzoylmethyl)-2-(phenylthio)tetrahydropyran (11c).** This compound was isolated as a solid, mp 87–88 °C: ^{1}H NMR ($CDCl_3$) δ 1.50–1.93 (m, 4 H), 2.79–2.91 (m, 1 H), 2.98 (dd, J = 7.2, 17.4 Hz, 1 H), 3.25 (dd, J = 6.0, 17.4 Hz, 1 H), 3.65–3.75 (m, 1 H), 4.26 (td, J = 2.7, 11.4 Hz, 1 H), 5.58 (d, J = 4.2 Hz, 1 H), 7.15–7.28 (m, 3 H), 7.39–7.50 (m, 4 H), 7.56 (t, J = 7.2 Hz, 1 H), 7.98 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 198.29, 131.13, 128.80, 128.55, 128.02, 126.69, 90.30, 60.95, 41.81, 36.89, 26.18, 25.36; CIMS (NH_3, solids probe) m/z (relative intensity) 330 (M + NH_4^+, 18), 313 (MH^+, 14), 203 (M^+ – SPh, 100). Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.03; H, 6.45; S, 10.26. Found: C, 72.91; H, 6.44; S, 10.06.

***cis*-3-(Benzoylmethyl)-2-(butylthio)tetrahydropyran (11d).** This compound was isolated as a liquid: ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.2 Hz, 3 H), 1.34 (sextet, J = 7.2 Hz, 2 H), 1.47–1.71 (m, 6 H), 2.45–2.61 (m, 2 H), 2.70–2.80 (m, 1 H), 2.85 (dd, J = 7.2, 17.1 Hz, 1 H), 3.14 (dd, J = 6.3, 17.1 Hz, 1 H), 3.55–3.63 (m, 1 H), 4.12 (dt, J = 2.7, 11.1 Hz, 1 H), 5.24 (d, J = 3.9 Hz, 1 H), 7.44 (t, J = 7.2 Hz, 2 H), 7.55 (t, J = 7.2 Hz), 7.96 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 198.59, 137.12, 132.98, 128.59, 127.93, 86.54, 60.56, 41.52, 36.29, 31.92, 30.14, 26.30, 25.01, 22.00, 13.62; GCMS m/z (relative intensity) 203 (M^+ – SBu, 83), 185 (5), 172 (13), 161 (4), 105 (100), 77 (24); HRMS m/z 292.1497 (calcd for $C_{17}H_{24}O_2S$ 292.1497).

3-(Acetylmethyl)-2-(phenylthio)tetrahydropyran (11b). Two isomers were isolated as liquids by column chromatography. Major isomer: ^{1}H NMR ($CDCl_3$) δ 1.40–1.56 (m, 1 H), 1.57–1.83 (m, 3 H), 2.15 (s, 3 H), 2.45 (dd, J = 6.0, 16.8 Hz, 1 H), 2.57–2.76 (m, 2 H), 3.63–3.72 (m, 1 H), 4.21 (dt, J = 3.0, 11.4 Hz, 1 H), 5.49 (d, J = 3.9 Hz, 1 H), 7.20 (t, J = 7.2 Hz, 1 H), 7.27 (t, J = 7.2 Hz, 2 H), 7.44 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 206.83, 135.11, 131.04, 128.84, 126.70, 89.84, 60.76, 46.80, 36.42, 30.63, 25.98, 25.30; GCMS m/z (relative intensity) 250 (M^+, 0.5), 141 (82), 123 (16), 111 (16), 99 (12), 81 (24), 43 (100); HRMS m/z 250.1026 (calcd for $C_{14}H_{18}O_2S$ 250.1028). Minor isomer: this compound could be isolated in only 70% purity (contaminated with the major isomer); ^{1}H NMR ($CDCl_3$) 1.30–1.50 (m, 1 H), 1.56–1.73 (m, 3 H), 2.14 (s, 3 H), 2.30–2.38 (m, 1 H), 2.44 (dd, J = 7.5, 16.8 Hz, 1 H), 2.95 (dd, J = 4.2, 16.8 Hz, 1 H), 3.50–3.60 (m, 1 H), 4.12–4.21 (m, 1 H), 4.84 (d, J = 6.6 Hz, 1 H), 7.19–7.31 (m, 3 H), 7.47 (d, J = 7.2 Hz, 2 H).

3-(Formylmethyl)-2-(phenylthio)tetrahydropyran (11a). Two isomers were isolated as liquids by column chromatography. Major isomer: ^{1}H NMR ($CDCl_3$) δ 1.44–1.84 (m, 4 H), 2.44–2.56 (m, 1 H), 2.62–2.79 (m, 2 H), 3.64–3.74 (m, 1 H), 4.23 (dt, J = 3.0, 11.4 Hz, 1 H), 5.47 (d, J = 3.9 Hz, 1 H), 7.21 (t, J = 6.9 Hz, 1 H), 7.28 (t, J = 6.9 Hz, 2 H), 7.43 (d, J = 7.2 Hz, 2 H), 9.77 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 206.87, 131.13, 129.01, 128.82, 126.97, 89.39, 65.45, 46.75, 35.37, 27.76, 23.66; GCMS m/z (relative intensity) 236 (M^+, 0.3), 127 (100), 109 (24), 97 (11), 81 (45); HRMS m/z 236.0873 (calcd for $C_{13}H_{16}O_2S$ 236.0871). Minor isomer: ^{1}H NMR ($CDCl_3$) δ 1.36–1.48 (m, 1 H), 1.62–1.72 (m, 2 H), 2.02–2.11 (m, 1 H), 2.30–2.42 (m, 1 H), 2.48 (ddd, J = 1.8, 7.2, 17.1 Hz, 1 H), 2.93 (ddd, J = 1.2, 5.1, 17.1 Hz, 1 H), 3.49–3.59 (m, 1 H), 4.12–4.22 (m, 1 H), 4.81 (d, J = 7.2 Hz, 1 H), 7.23–7.34 (m, 3 H), 7.48 (d, J = 7.2 Hz, 2 H), 9.75 (s, 1 H); GCMS m/z (relative intensity) 236 (M^+, 0.3), 127 (100), 109 (26), 97 (17), 81 (47).

1-(Benzoylmethyl)-2,2-bis(phenylthio)cyclohexane (15a). This compound was isolated as an oil: ^{1}H NMR ($CDCl_3$) δ 1.00–2.00 (m, 8 H), 2.63 (dd, J = 8.7, 15.3 Hz, 1 H), 3.17 (dd, J = 10.5, 17.7 Hz, 1 H), 4.20 (d, J = 17.7 Hz, 1 H), 7.20–7.45 (m, 8 H), 7.50 (t, J = 7.2 Hz, 2 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.81 (d, J = 7.8 Hz, 2 H), 8.08 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 199.33, 137.60, 137.51, 137.28, 133.00, 131.30, 129.95, 129.21, 129.10, 128.80, 128.60, 128.54, 128.12, 70.75, 41.38, 40.84, 36.08, 29.10, 25.40, 22.65. Anal. Calcd for $C_{26}H_{26}OS_2$: C, 74.41; H, 6.49; S, 15.29. Found: C, 74.15; H, 6.50; S, 16.45. Compound **15** on hydrolysis with $HgCl_2$ in CH_3CN (25%) at gentle reflux for 6 h gave **10c**.

3-(Benzoylmethyl)-2-(phenylthio)cyclohexene (17a). This compound was identified by GCMS only because of separation problems: GCMS m/z (relative intensity) 308 (M^+, 6), 199 (18), 188 (100), 155 (9), 105 (35), 77 (33). After separation of the thioacetal **15a** by column chromatography from the reaction mixture the inseparable mixture of **17a** and **6a** was hydrolyzed with $HgCl_2$ in CH_3CN (75%)–H_2O (25%) at gentle reflux for 6 h to convert **17a** into **10c** whose yield was determined by GC.

1-(Benzoylmethyl)-2-(butylthio)-2-(phenylthio)cyclohexane (15b). This compound was isolated as an inseparable mixture of two diastereomers in approximately a 5:1 ratio: ^{1}H NMR ($CDCl_3$) (only peaks of the major isomer are given) δ 0.98 (t, J = 7.2 Hz, 3 H), 1.35–1.85 (m, 11 H), 2.05 (br d, J = 14.4 Hz, 1 H), 2.53–2.69 (m, 2 H), 2.79 (dd, J = 6.6, 8.1 Hz, 1 H), 2.82 (dd, J = 6.9, 7.8 Hz, 1 H), 3.06 (dd, J = 7.2, 17.4 Hz, 1 H), 4.03 (dd, J = 1.8, 17.4 Hz, 1 H), 7.28–7.60 (m, 8 H), 8.05 (d, J = 7.2 Hz, 2 H); CIMS (NH_3, solids probe) m/z (relative intensity) 416 (M + NH_4^+, 1), 309 (M^+ – SBu, 24), 289 (M^+ – SPh, 100). Compound **15b** on hydrolysis with $HgCl_2$ in CH_3CN (75%)–H_2O (25%) at gentle reflux for 6 h gave the diketone **10c**.

3-(Benzoylmethyl)-2-(butylthio)cyclohexene (17b). This compound was identified by GCMS only due to separation problems: GCMS m/z (relative intensity) 288 (M^+, 6), 199 (4), 168 (86), 112 (100), 105 (48), 91 (7), 77 (47).

1-Phenylpent-4-en-1-one (19).[46] This compound was isolated as a liquid: ^{1}H NMR ($CDCl_3$) δ 2.43–2.48 (m, 2 H), 3.02–3.07 (m, 2 H), 5.00–5.08 (m, 2 H), 5.82–6.00 (m, 2 H), 7.40–7.60 (m, 3 H), 7.90–8.20 (br d, J = 7.2 Hz, 2 H); GCMS m/z (relative intensity) 160 (M^+, 2), 115 (1), 105 (100), 77 (46). The ^{1}H NMR compared favorably with that given in the literature.[46]

1-Butoxy-2-(phenylsulfonyl)-1-(phenylthio)ethane. This compound was isolated as an oil: ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J = 7.2 Hz, 3 H), 1.20 (apparent sextet, J = 7.2 Hz, 2 H), 1.27–1.39 (m, 2 H), 3.30 (td, J = 6.3, 9.0 Hz, 1 H), 3.88 (td, J = 6.9, 9.0 Hz, 1 H), 5.11 (dd, J = 5.4, 6.9 Hz, 1 H), 7.25–7.33 (m, 3 H), 7.35–7.41 (m, 2 H), 7.51 (t, J = 7.5 Hz, 2 H), 7.62 (t, J = 7.5 Hz, 1 H), 7.82 (d, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 140.12, 134.46, 133.43, 130.45, 129.03, 128.92, 128.54, 127.92, 82.09, 68.88, 62.22, 30.91, 19.15, 13.84; HRMS m/z 350.101 (calcd for $C_{18}H_{22}O_5S_2$ 350.1010).

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Supplementary Material Available: ^{1}H NMR spectra for all new isolated title compounds (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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