Cyclizations in the Addition of Alkylmercury Halides to Dienes and Enynes

Glen A. Russell,* Chaozhong Li, and Ping Chen

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received January 19, 1996[⊗]

Abstract: Photostimulated additions of *tert*-butylmercury halides to 1,6-dienes and enynes, including $(CH_2{=}CHCH_2)_2X$ with X = CH_2, $C(COEt)_2$, O, or $NCH_2CH{=}CH_2$, form the primary alkylmercury halides resulting from 5-exo-cyclizations of the adduct radicals, *t*-$BuCH_2CH^{\bullet}CH_2XCH_2CH{=}CH_2$. The kinetic chain lengths of these free-radical processes are low and in the range of 3−7 at 35 °C in Me_2SO. 5-Exo-cyclizations with kinetic chain lengths of ∼100 are observed in the photostimulated addition of *t*-BuHgI to $CH_2{=}CHP(O)(OR)OCH_2CH{=}CH_2$ (R = H or allyl), $CH_2{=}CHC(O)N(R)CH_2CH{=}CH_2$ (R = Me, Ph, or $CH_2CH{=}CH_2$), or $CH_2{=}CHC(O)OC(Me)_2CH{=}CH_2$. The radicals *t*-$BuCH_2CH^{\bullet}C(O)C(Me)_2(CH_2)_nCH{=}CH_2$ cyclize mainly in the 6-endo mode for $n = 1$ and more rapidly in the 6-exo mode for $n = 2$, while the radicals *t*-$BuCH_2CH^{\bullet}C(O)OC(Me)_2(CH_2)_nCH{=}CH_2$ cyclize only in the exo mode for $n = 0$ or 1 but with a faster rate for 5-exo-cyclization. *Gem*-dimethyl substitution adjacent to the alkyl oxygen accelerates the 5-exo-cyclization of the ester radicals because of rotamer populations but retards their 6-exo-cyclization because of the boatlike transition state required to maintain planarity of the ester function in forming a δ-lactone.

Introduction

The photostimulated free-radical additions of RHgCl across the double bonds of the electronegatively substituted alkenes $CH_2{=}CHP(O)(OEt)_2$ and $CH_2{=}CHSO_2Ph$ occur readily.[1] Under the conditions employed kinetic chain lengths of ∼100 were observed at 35 °C in PhH or Me_2SO for the propagation sequence of reactions 1 and 2 with R = *t*-Bu. The reaction is

$$R^{\bullet} + CH_2{=}CHZ \rightarrow RCH_2CHZ^{\bullet} \quad (1)$$

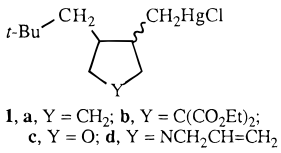
$$RCH_2CHZ^{\bullet} + RHgCl \rightarrow RCH_2CH(Z)HgCl + R^{\bullet} \quad (2)$$

dependent upon the nature of Z since with Z = Bu the kinetic chain length is only 1.4 while with Z = CO_2R or CN the adduct is not formed from *t*-BuHgCl or *t*-BuHgI because the resonance-stabilized adduct radical fails to participate in reaction 2. However, the adduct mercurials with Z = CO_2R, $CONR_2$, or CN as well as $(EtO)_2PO$ and $PhSO_2$ can be prepared in high yield in a radical chain process by reaction of the substituted alkene with *t*-BuHgI/KI in Me_2SO solution in the dark at room temperature.[2] Yields are typically 95% in a 30 min reaction using 1.2 equiv of *t*-BuHgI. Iodide increases the rate of thermal initiation, possibly by the formation of $(t\text{-Bu})_2Hg$, while the ate-complex (t-$BuHgI_2^-$) is a better trap than *t*-BuHgI for an enolyl-type adduct radical.[2,3]

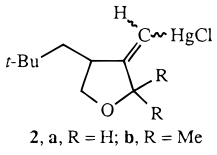
In hopes of increasing the kinetic chain length and product yields in the addition of *t*-BuHgX to alkenes, we have examined reactions of 1,6-dienes and enynes including acrylates, *N*-allylacrylamides, and vinyl ketones where the initial adduct radicals can undergo cyclization to produce radicals that should be more reactive in reaction 2 than secondary alkyl or enolyl-type radicals.[4] In addition, the iodide-promoted reactions of *t*-BuHgI with α,β-unsaturated systems has been utilized to achieve cyclizations for allyl vinylphosphonates, allyl and homoallyl acrylates, *N*-allylacrylamides, and alkenyl vinyl ketones.

Results and Discussion

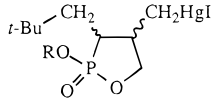
5-Exo-Cyclizations of 1,6-Hexadienes. As expected, only cyclized products are observed upon photolysis of *t*-BuHgX with the dienes and enyne of Table 1. The products **1** and **2** are formed in good yields and with longer kinetic chain lengths than observed for 1-hexene. However, the initial chain lengths are modest (∼3−7), reflecting the low reactivity of an unactivated terminal alkene toward *t*-Bu$^{\bullet}$.[1] Reactions of allyl vinylphosphonates to form **3** occur more readily, and with *t*-BuHgI a kinetic chain length of 67 was measured for the formation of **3a**. The fast reactions observed reflect the fact that electronegatively substituted alkenes, e.g., Z = CN, CO_2R, or $P(O)(OEt)_2$ in reaction 1, are 10^2−10^3 more reactive toward *t*-Bu$^{\bullet}$ than unactivated terminal alkenes.[1]



1, **a**, Y = CH_2; **b**, Y = $C(CO_2Et)_2$; **c**, Y = O; **d**, Y = $NCH_2CH{=}CH_2$



2, **a**, R = H; **b**, R = Me



3, **a**, R = H; **b**, R = $CH_2CH{=}CH_2$

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

(1) Russell, G. A.; Shi, B. Z.; Kim, B. H.; Jiang, W.; Hu, S.; Baik, W. *J. Am. Chem. Soc.* **1995**, *117*, 3952.

(2) (a) Russell, G. A.; Li, C.; Chen, P. *J. Am. Chem. Soc.* **1995**, *117*, 3645. (b) Russell, G. A.; Chen, P.; Yao, C.-F.; Kim, B. H. *J. Am. Chem. Soc.* **1995**, *117*, 5967. (c) Russell, G. A.; Li, C. *Synlett* **1996**, 699.

(3) Russell, G. A.; Hu, S.; Herron, S.; Baik, W.; Ngoviwatchai, P.; Jiang, W.; Nebgen, M.; Wu, Y.-W. *J. Phys. Org. Chem.* **1988**, *1*, 299.

(4) For reviews of the homolytic addition reactions of 1,6-dienes see: Wilt, J. W. in *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 7. Abell, P. I. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 13. Curran, D. P.; Porter, N. A.; Giese, B. *Stereochemistry of Radical Reactions*; VCH: Weinheim, 1996; Chapter 2.

S0002-7863(96)00189-8 CCC: $12.00

Table 1. Photostimulated Reactions of *t*-BuHgX with Dienes in Me_2SO at 35 °C[a]

substrate	*t*-BuHgX X, equiv	time, h	product (%)	cis/trans	kcl[b]
$CH_2{=}CH(CH_2)_3CH{=}CH_2$	Cl, 2	6	**1a** (86)	5	3.3
$CH_2{=}CHCH_2C(CO_2Et)_2CH_2CH{=}CH_2$	Cl, 2	6	**1b** (95)	8	6.6
$CH_2{=}CHCH_2OCH_2CH{=}CH_2$	Cl, 2	6	**1c** (98)	4	6.5
$CH_2{=}CHCH_2N(CH_2CH{=}CH_2)_2$	Cl, 2	6	**1d** (73)	6	
$CH_2{=}CHCH_2OCH_2C{\equiv}CH$	Cl, 2	11	**2a** (56)		4.2
$CH_2{=}CHCH_2OC(Me)_2C{\equiv}CH$	Cl, 2	5	**2b** (75)	*c*	
$CH_2{=}CHP(O)(OH)OCH_2CH{=}CH_2$	I, 1.2[d]	1	**3a** (87)	1	4300
$CH_2{=}CHP(O)(OH)OCH_2CH{=}CH_2$	I, 1.2	0.75	**3a**(91)	1	67
$CH_2{=}CHP(O)(OCH_2CH{=}CH_2)_2$	I, 1.1	4	**3b**(80)	*e*	

[a] Photolysis with a 275 W fluorescent sunlamp. [b] The initial kinetic length measured by the $(t\text{-Bu})_2NO^{\bullet}$ method[1] with a diene concentration of 0.1 M. [c] Z/E = 1:1.5. [d] Dark reaction in the presence of 4 equiv of NH_4I. [e] A mixture of three diastereomers in a 1:1:1 ratio.

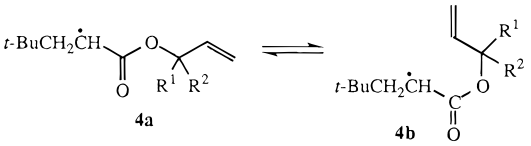
Table 2. Photostimulated Reactions of RHgX with Allyl Acrylates and Acrylamides in Me_2SO at 35 °C[a]

substrate	*t*-BuHgX X, equiv	time, h	product (%)	trans/cis	kcl[b]
$CH_2{=}CHC(O)OC(Me)_2CH{=}CH_2$	I, 2	0.2	**5c** (65)	> 50	85
$CH_2{=}CHC(O)OC(Me)_2CH{=}CH_2$	Cl, 2	0.3	**5c** (65)	> 50	35
$CH_2{=}CHC(O)OC(Me)_2C{\equiv}CH$	I, 2	0.2	**6** (55)	*c*	50
$CH_2{=}CHC(O)N(Me)CH_2CH{=}CH_2$	I, 2	4	**7a** (55)	> 50	
$CH_2{=}CHC(O)N(Ph)CH_2CH{=}CH_2$	Cl, 2	0.8	**7b** (95)	> 50	
$CH_2{=}CHC(O)N(CH_2CH{=}CH_2)_2$	Cl, 2	0.3	**7c** (85)	> 50	210
$CH_2{=}CHC(O)N(CH_2CH{=}CH_2)_2$	*i*-PrHgCl, 2	2	*d* (89)	10	75

[a] Photolysis with a 275 W fluorescent sunlamp. [b] The initial kinetic length measured by the $(t\text{-Bu})_2NO^{\bullet}$ method[1] with a diene concentration of 0.1 M. [c] *E* and *Z* isomers (unassigned) in a 20:35 ratio. [d] The isopropyl analog of **7c**.

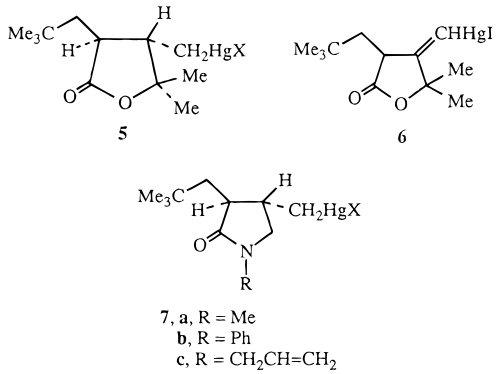
As expected, mixtures of cis and trans isomers of **1** and **3** are formed; see Table 1. The mercurials **1**−**3** underwent reaction with 2 equiv of Ph_2S_2 upon photolysis to form the corresponding phenyl sulfides (substitution of PhS for HgCl) in quantitative yield and could be reduced by $NaBH_4$ to give the methyl or methylene derivatives.

5-Exo-Cyclizations Leading to Lactones and Lactams, a. *t*-BuHgX/*hν*. Cyclization in radical addition to allyl acrylates is not usually observed, e.g., with tosyl halides,[5] although cyclization is observed in the addition of Bu_3SnH to allyl propiolates.[6] A few examples of 5-exo-cyclizations of radicals derived from terminally substituted allyl or propargyl esters of α-halo carboxylic acids have been reported for Bu_3SnH reactions,[7,8] but for cyclization to occur low concentrations of Bu_3SnH and elevated temperatures are required. Ester radicals such as **4** undergo slow cyclization in part because the preferred rotamer is the s-trans conformation **4a**, whereas cyclization requires the s-cis rotamer, **4b**.[9] For example, with methyl



acetate the s-trans (*Z*) conformation is ∼8.5 kcal/mol more stable than the s-cis conformer (*E*), and a barrier of 10−15 kcal/mol is estimated for the *Z* to *E* conversion.[10] Nevertheless, cyclizations of ester radicals to form γ-lactones does occur readily in the Mn(III) oxidation of allylic β-diesters[11] and in the halogen-atom transfer cyclization of allylic esters of α-halo carboxylic acids at 80 °C.[9,12]

Photolysis of *t*-BuHgI with allyl acrylate produces only ∼10% of the cyclized organomercurial with the adduct radical **4** ($R^1 = R^2 = H$) mainly forming telomerization and reduction products. However, upon *gem*-dimethyl substitution (**4**, $R^1 = R^2 = Me$), cyclization occurs readily to form **5** with a kinetic chain length > 80 (Table 2), while the corresponding propargyl ester forms **6**. The dramatic effect of *gem*-dimethyl substitution on the rate of 5-exo-cyclization involves angle compression effects (Thorpe−Ingold effect) as well as rotamer populations and a reduced barrier of the s-trans to s-cis interconversion of the radical **4**.[13]



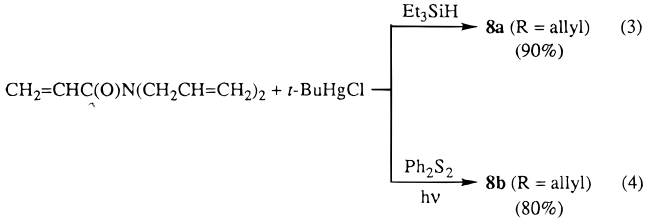
The structure of **5** was assigned from the NOESY spectrum of the phenylthiyl substitution product isolated as a single

(5) For a review of tosyl halide radical additions see: Betrand, M. P. *Org. Prep. Procedure Int.* **1994**, *26*, 257.
(6) Lee, E.; Ko, S. B.; Jung, K. W.; Chang, M. H. *Tetrahedron Lett.* **1989**, *30*, 827.
(7) Ihara, M.; Taniguchi, N.; Fukumoto, K.; Kametani, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1438. Belletire, J. L.; Mahmoodi, N. O. *Tetrahedron Lett.* **1984**, *30*, 4363. Hanessian, S.; Di Fabio, R.; Marcoux, J.-F.; Prod'homme, M. *J. Org. Chem.* **1990**, *55*, 3436.
(8) Clough, J. M.; Pattenden, G.; Wight, P. C. *Tetrahedron Lett.* **1989**, *30*, 7469.
(9) Curran, D. P.; Tamine, J. *J. Org. Chem.* **1991**, *56*, 2746.
(10) Blown, C. E.; Günthard, H. H. *Chem. Phys. Lett.* **1981**, *84*, 2673. Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935.
(11) Corey, E. J.; Kang, M. *J. Am. Chem. Soc.* **1984**, *106*, 5384. Ourmar-Mahimat, H.; Moustrou, C.; Suzur, J.-M.; Bertrand, M. P. *J. Org. Chem.* **1989**, *54*, 5684. Snider, B. *Chem. Rev.* **1996**, *96*, 339.
(12) Curran, D. F.; Chang, C.-T. *Tetrahedron Lett.* **1987**, *28*, 2477. Curran, D. F.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140. Barth, F.; O-Yang, C. *Tetrahedron Lett.* **1990**, *31*, 1121. Nagashima, N. Seki, K.; Ozaki, N.; Wakamatsu, H.; Itoh, K.; Tomo, Y.; Tsuji, J. *J. Org. Chem.* **1990**, *55*, 985.
(13) Jung, M. E.; Gervoy, J. *J. Am. Chem. Soc.* **1991**, *113*, 224. Jung, M. E.; Trifunovich, I. D.; Lensen, N. *Tetrahedron Lett.* **1992**, *33*, 6719.

diastereomer upon photolysis with Ph_2S_2. Reduction of **5** with $NaBH_4$ forms the expected β-methyl-substituted γ-butyrolactones, but **6** led to the rearranged α,β-unsaturated lactone. The facile rearrangement of 4-ylidenebutyrolactones to α,β-unsaturated lactones has been previously observed.[8] In a similar fashion, photolysis of **6** with Ph_2S_2 formed the rearranged 3-(2,2-dimethylpropyl)-5,5-dimethyl-4-[(phenylthio)methyl]-2(5*H*)-furanone.

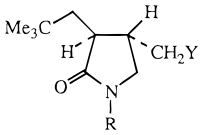
N-Allylacrylamide fails to form the cyclized mercurial upon irradiation with *t*-BuHgI while the *N*-methyl, *N*-phenyl, and *N*,*N*-diallyl derivatives form the lactams **7**. The importance of a second substituent on nitrogen in facilitating ring closure of α-carbamoyl radicals has been previously noted for Bu_3SnH reactions and again appears to reflect rotamer populations and the barriers to their interconversion.[9,14,15] Cyclization to form **7c** was expected because one of the allyl groups will always be present in the s-cis amide conformation.[9] However, cyclization to yield **7b** at 35 °C was unexpected in view of the fact that in $PhN(CH_3)COMe$ the rotamer with the phenyl and carbonyl oxygen in a transoid arrangement is preferred by 3.5 kcal/mol[16] and rotation around the amide bond is typically 16−22 kcal/mol,[9] although the barrier to rotation may be less in the adduct radical. The ^1H NMR spectrum of $CH_2{=}CHC(O)N(Me)CH_2CH{=}CH_2$ at room temperature shows two rotamers with about equal populations while the *N*-phenyl derivative shows only a single *N*-allyl resonance. The (*E*)-conformation is highly preferred as evidenced by NOE between the acryoyl −CH= proton (δ 6.0, dd) and an aromatic proton but not with the allyl methylene group. The lactams **7b,c** are formed as single diastereomers whose trans structure was demonstrated by ^1H NOESY. However, with *i*-Pr as the adding radical the analogous product to **7c** is formed as a 9:1 ratio of trans and cis isomers, and with Bu• as the adding radical even more of the cis isomer is formed.

The cyclization of $t\text{-}BuCH_2CH^{\bullet}C(O)N(CH_2CH{=}CH_2)_2$ is so fast that only the trans-cyclized products are formed in three-component cyclizations using excess (4 equiv) *t*-BuHgCl and Et_3SiH or Ph_2S_2, reactions 3 and 4. The *tert*-butyl groups are



not used efficiently in reactions 3 and 4 because of competing reactions of *t*-Bu• leading to *t*-BuSPh or *t*-BuH. A higher efficiency is observed by first forming **7** and, without isolation, treating **7** with Et_3SiH or photolyzing with Ph_2S_2. Thus, photolysis of **7c** with 2 equiv of Et_3SiH, Ph_2S_2, Ph_2Se_2, I_2, or $CH_2{=}CHCH_2SPh$ forms **8a**−**e** (R = allyl) in yields of ∼80% based on the starting acrylamide.

b. Dark Reactions with *t*-BuHgI$_2^-$. Reactions of acrylic esters or acrylamides with a mixture of *t*-BuHgI (1.2 equiv) and KI (2−4 equiv) in Me_2SO in the dark at room temperature



8, a, Y = H
b, Y = SPh
c, Y = SePh
d, Y = I
e, Y = $CH_2CH{=}CH_2$

form the 1:1 adducts in 90−95% yield.[2] The reactions are inhibited for days by 10 mol % of $(t\text{-}Bu)_2NO^{\bullet}$ with measured kinetic chain lengths of ∼5000 for methyl and allyl acrylates. With allyl vinylphosphonate a similar dramatic increase in reaction rate upon addition of KI is observed (Table 1) in a reaction leading to **3a** with a kinetic chain length of 4300. In a similar fashion, 0.1 M $CH_2{=}CHC(O)N(CH_2CH{=}CH_2)_2$ forms **7c** (X = I) in essentially quantitative yield in a 10 min dark reaction that is inhibited by 10 mol % of $(t\text{-}Bu)_2NO^{\bullet}$ for 2 weeks (kinetic chain length ∼20 000).[17] With adduct radicals that cyclize less readily, the uncyclized adducts are also formed. Thus, in a 30 min reaction under the conditions employed for *N*,*N*-diallylacrylamide, *N*-allylacrylamide forms only the uncyclized adduct ($t\text{-}BuCH_2CH(HgI)NHCH_2CH{=}CH_2$) but $CH_2{=}CHC(O)N(Me)CH_2CH{=}CH_2$ gives 58% of **7a** and 42% of the uncyclized adduct while the *N*-phenyl derivatives forms 65% of **7b** and 29% of the uncyclized adduct.[18] The uncyclized organomercurial adducts slowly isomerize to **7a,b** in the dark and more rapidly upon photolysis. When NH_4I is substituted for KI the uncyclized organomercurials are rapidly protonolized to yield the reductive alkylation products with $CH_2{=}CHC(O)NHCH_2CH{=}CH_2$ yielding only $t\text{-}BuCH_2CH_2C(O)NHCH_2CH{=}CH_2$ and $CH_2{=}CHC(O)N(CH_2CH{=}CH_2)_2$ yielding only **7c** but $CH_2{=}CHC(O)N(Ph)CH_2CH{=}CH_2$ yielding a mixture of 60% **7b** and 35% of $t\text{-}BuCH_2CH_2C(O)N(Ph)CH_2CH{=}CH_2$. However, with Ph_2S_2, $BrCCl_3$, or $CH_2{=}CHCH_2SPh$ photolysis of the mixture of **7b** and its uncyclized isomer forms only the cyclized products **8b,d,e** (R = Ph) in yields of 85, 85, and 65%, respectively. Reaction with $BrCCl_3$ presumably forms **8** with Y = Br, which undergoes an S_N2 reaction with I^- to form **8d**. Similarly, photolysis of **7a** and its uncyclized isomer with 2 equiv of Ph_2S_2 forms **8b** (R = Me) in 90% yield. Other reagents more reactive toward α-carbamoyl radicals (e.g., Ph_2Se_2) yield mixtures of cyclized and uncyclized products.

Reactions of allyl and homoallyl acrylates with *t*-BuHgI (1.2 equiv) and KI (3 equiv) in Me_2SO form the adduct mercurials in yields of 85−95% in 30 min in the dark. Only the acyclic mercurials **9a,b** are formed from allyl and 1-methylallyl acrylates. However, 0.1 M $CH_2{=}CHC(O)OC(Me)_2CH{=}CH_2$ forms a mixture of uncyclized (**9c**, 45%) and cyclized (**5**, 40%) mercurials; with NH_4I in place of KI the yield of **5** is reduced to 30% and 65% of $t\text{-}BuCH_2CH_2CO_2(Me)_2CH{=}CH_2$ is formed. The homoallyl acrylates with or without *gem*-dimethyl substitution form only the acyclic adducts **9d**−**f**. In the presence of NH_4I the mercurials **9a,b,d**−**g** yield the uncyclized protonolysis products in essentially quantitative yield.

Cyclization Products from Acyclic Organomercurials. Reaction of *t*-BuHgI/KI with allyl acrylates produces more of

(14) Stock, G.; Mah, R. *Heterocycles* **1989**, *28*, 723. Sato, T.; Wado, Y.; Nishimoto, N.; Ishibashi, H.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1* **1989**, 879.

(15) 5-Exo cyclization of α-carbamoyl radicals derived from secondary amides occurs in halogen-transfer cyclizations at 140 °C: Nagashima, H.; Ara, K.; Wakamatsu, H.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1985**, 518. Cyclization of $CH_3CH^{\bullet}CONHC(R^1)(R^2)C{\equiv}CH$ has been observed in the presence of Bu_3SnH but only when $R^1 = R^2$ = alkyl.[8]

(16) Saito, S.; Toriumi, Y.; Tomioka, N.; Itai, A. *J. Org. Chem.* **1995**, *60*, 4715.

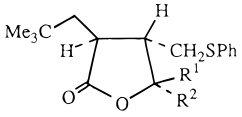
(17) All attempts to achieve cyclization failed using *t*-BuBr/hν at 40 °C or *t*-BuBr/AlBN at 60 °C.

(18) Apparently, rotation around the amide bond in $t\text{-}BuCH_2CH^{\bullet}CHC(O)N(Ph)CH_2CH{=}CH_2$ occurs rapidly at 25 °C with the normal amide barrier greatly reduced by delocalization in the α-carbamoyl radical. In refluxing toluene this rotation occurs more readily than reaction with Bu_3SnD as evidenced by the high yield of 5-exo cyclization product from $Me_2C^{\bullet}C(O)N(Ph)CH_2CH{=}CH_2$: Jones, K.; Storey, J. M. D. *J. Chem. Soc., Chem. Commun.* **1992**, 1766.

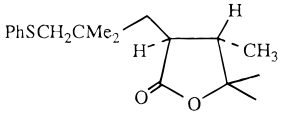
t-$BuCH_2CH(HgI)C(O)OC(R^1)(R^2)(CH_2)_nCH{=}CH_2$

9a, $R^1 = R^2$ H, $n = 0$
b, R^1 = Me, R^2 = H, $n = 0$
c, $R^1 = R^2$ = Me, $n = 0$
d, $R^1 = R^2$ = H, $n = 1$
e, R^1 = Me, R^2 = H, $n = 1$
f, $R^1 = R^2$ = Me, $n = 1$
g, $R^1 = CH{=}CH_2$, R^2 = H, $n = 0$
h, $R^1 = CH_2CH{=}CH_2$, R^2 = Me, $n = 0$
i, $R^1 = R^2 = CH_2CH{=}CH_2$, $n = 0$
j, $R^1 = CH_2CH_2CH{=}CH_2$, R^2 = H, $n = 0$
k, $R^1 = CH_2CH_2CH{=}CH_2$, R^2 = Me, $n =$
l, $R^1 = CH_2CH_2CH{=}CMe_2$, R^2 = Me, $n = 0$

the uncyclized adducts than photolysis with *t*-BuHgX because *t*-$BuHgI_2^-$ is more efficient in trapping the uncyclized enoyl-type radical.[19] However, because of the rapidity with which *t*-$BuHgI_2^-$ reacts with α,β-unsaturated systems, it is often advantageous to conduct cyclizations in a two-step fashion without isolation of intermediates such as **9**. Furthermore, in this manner it is possible to generate the adduct radicals from **9** in the absence of the α,β-unsaturated substrate or of excess *t*-BuHgX. Electrophilic radicals, such as α-keto, α-carboalkoxy, or α-carbamoyl radicals, react slowly with disulfides while nucleophilic alkyl radicals readily undergo S_H2 substitution at sulfur.[19,20] Thus, photolysis of **9** with 2 equiv of Ph_2S_2 can be an excellent route to the cyclized phenyl sulfides in a two-step process not requiring the isolation of **9**, Scheme 1. Although photolysis of *t*-$BuCH_2CH(HgI)C(O)NHCH_2CH{=}CH_2$ with 2 equiv of Ph_2S_2 forms only *t*-$BuCH_2CH(SPh)C(O)NHCH_2$-$CH{=}CH_2$, **9a** gives a good yield (65%) of the cyclized sulfide **10a**. In a similar fashion **9b** is converted to **10b** (50%) while

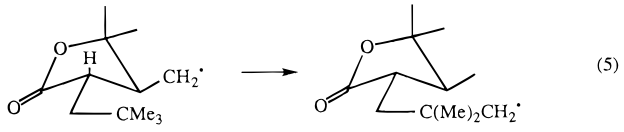


10, **a**, $R^1 = R^2$ = H
b, R^1 = Me, R^2 = H
c, $R^1 = R^2$ = Me



11

photolysis of **5** (or a mixture of **5** and **9c** formed in the presence of I^-) with 0.2 M Ph_2S_2 forms 55% of **10c** and 16% of **11**, apparently from the intramolecular hydrogen atom transfer of reaction 5. Doubling the concentration of Ph_2S_2 increases the



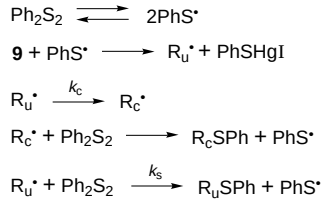
(5)

yield of **10c** to 66% and decreases the yield of **11** to 10% with the formation of no more than 2% of the uncyclized sulfide.

(19) Trapping of the cyclized radicals in the *t*-BuHgI/KI system presumably involves displacement of *t*-Bu• from *t*-BuHgI (the complexation constant for *t*-BuHgI + I^- in Me_2SO at 25 °C is ~1).[3] Since telomerization products are not observed in the iodide-promoted addition to acrylate esters with only a modest excess of *t*-BuHgI, it follows from the known k_p for methyl acrylate (7×10^2 at 30 °C) that trapping of *t*-$BuCH_2CH^{\bullet}CO_2R$ by *t*-$BuHgI_2^-$ at 25 °C has a rate constant in excess of 10^5 L/mol s and k_c for *t*-$BuCH_2CH^{\bullet}C(O)OCMe_2CH_2CH{=}CH_2$ is in the range of 10^6 s^{-1} with k_s no more than 10^3 L/mol s. *t*-Bu• is trapped by Ph_2S_2 with a rate constant of 1.3×10^6 and by BuSSBu with $k = 2.4 \times 10^4$ L/mol s at 40 °C: Russell, G. A.; Ngoviwatchai, P.; Tashtoush, H. I.; Pla-Dalmau, A.; Khanna, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 3530.

(20) Russell, G. A.; Kulkarni, S. V. *J. Org. Chem.* **1993**, *58*, 2678.

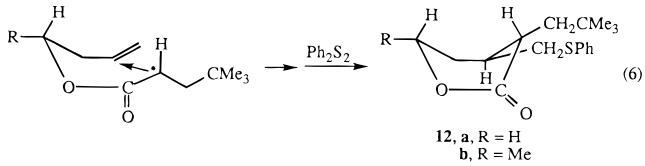
Scheme 1[a]



[a] $R_u^{\bullet}$ and $R_u^{\bullet}$ are uncyclized and cyclized radicals.

The initially formed cyclized radical apparently reacts slowly with Ph_2S_2 because of steric hindrance and has a puckered conformation so that the α and β trans substituents are quasiequatorial. This gives rise to an unusually large ^1H NMR coupling between the α and β methine hydrogens of ~12 Hz in **5**, **10c**, or **11** and allows the unexpected 1,6-hydrogen atom transfer of reaction 5 to occur.

Radical **4** ($R^1 = R^2$ = H) when formed in the absence of allyl acrylate or *t*-BuHgI, will undergo cyclization although the rate of cyclization must be relatively slow. Cyclization is even slower for the radicals derived from homoallylic acrylates via the organomercurials **9d**−**f**. The mercurials **9d,e** give the 6-exo-cyclization products **12a,b** in low yield upon photolysis with Ph_2S_2 while cyclization is not detected for **9f**. The sulfide **12b** is formed as a single diastereomer in which the methyl and neopentyl groups are cis to each other and trans to the $PhSCH_2$ substituent. Compound **12b** exists in a boat conformation as evidenced by NOE between the α and δ methine hydrogen atoms. The stereochemistry of **12b**, and the observation that *gem*-dimethyl alkylation in **9f** decreases the ease of cyclization, are consistent with a boatlike transition state for the 6-exo-cyclization of α-carboalkoxy radicals, reaction 6. The boat

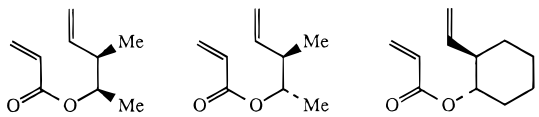


12, **a**, R = H
b, R = Me

(6)

conformation is apparently required to maintain the planarity of the ester function. Since an endo methyl substituent adjacent to the alkyl oxygen would introduce considerable strain in **12**, the radical derived from **9f** does not cyclize while **9e** leads only to a stereoisomer with the methyl and neopentyl groups in a cis arrangement. It is well known that δ-lactones do not exist in chair conformations[21] and, in contrast to γ-lactones, possess strain energies greater than those of the hydrocarbon, ether, or ketone.[22]

Further evidence in favor of a boatlike transition state for 6-exo-cyclization was obtained for the reactions of **13**−**15**.



13 **14** **15**

These acrylates form the uncyclized mercurials in high yield upon reaction with *t*-BuHgI/KI and give the expected proto-nolysis products in the presence of NH_4I. The mercurial from

(21) Philip, T.; Cook, R. L.; Malloy, T. B.; Allinger, N. L.; Chang, S.; Yuh, Y. *J. Am. Chem. Soc.* **1981**, *103*, 2151.

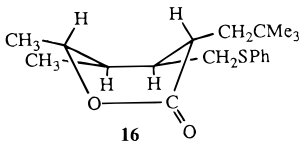
(22) Brown, J. M.; Conn, A. D.; Pilcher, G.; Leitao, M. L. P.; Yang, M.-Y. *J. Chem. Soc. Chem. Commun.* **1989**, 1817.

Table 3. Values of k_c/k_s in Me_2SO at 35 °C for Radicals Derived from **9** with the Yield of R_c-SPh in Parentheses for 0.2 M Ph_2S_2

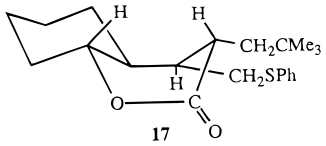
substituents	$n = 0$ (5-exo)	$n = 1$ (6-exo)	$n = 2$ (8-endo)
$R^1 = R^2 = H$	0.6 (65)	0.1 (9)	4.0 (35)
$R^1 = Me$, $R^2 = H$	2.2 (50)	0.6 (25)	11 (65)
$R^1 = R^2 = Me$	>20[a] (55)[b]	<0.05 (<5)	0.8 (31)

[a] Observed in the photolysis of the acrylate with *t*-BuHgI and Ph_2S_2. [b] 16% of **11** also formed.

13 fails to yield a cyclized sulfide upon photolysis with Ph_2S_2 while **14** and **15** are converted to **16** (50%) and **17** (53%). For



16



17

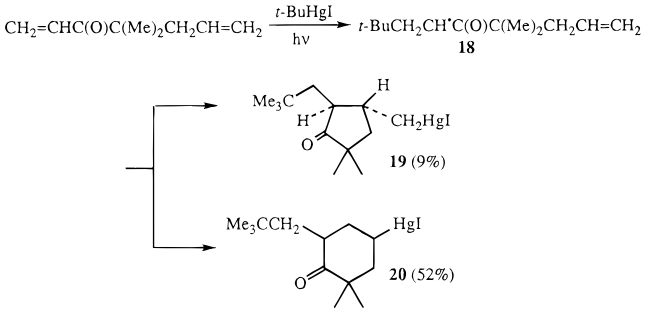
6-exo-cyclization of ester radicals to occur the alkyl substituents should occupy quasiequatorial positions in the boat transition state as is possible for the threo isomer **14** but not for the erythro isomer **13**.

Uncyclized sulfides are formed in the reaction of **9** with Ph_2S_2 when the radicals cyclize slowly. From the observed ratios of cyclized (R_cSPh) and uncyclized (R_uSPh) products the values of k_c/k_s (Scheme 1) can be obtained. Table 3 lists the values of k_c/k_s thus obtained and in parentheses the yields of the cyclized sulfides **10** or **12** observed with 0.2 M Ph_2S_2. Also included in Table 3 are the results for **9** with $n = 2$ which forms only the 8-endo-cyclization products.[23]

Since k_s should be fairly insensitive to the structure of the alkenyl portion of the ester, the values of k_c/k_s in Table 3 are considered to be a reasonable measure of the relative rates of cyclization of the α-carboalkoxy radicals derived from **9**.

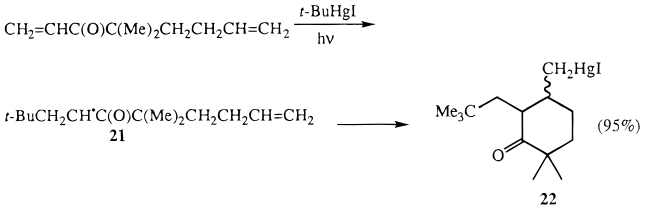
Cyclizations of α-Keto Radicals to Cycloalkanones. α-Keto radicals (e.g., $CH_2{=}CH(CH_2)_nC(O)CH_2^{\bullet}$) are known to cyclize preferentially in the 6-endo and to a significant extent in the 7-endo fashion.[12,24,25] At 35 °C photolysis of $CH_2{=}CHC(O)C(Me)_2CH_2CH{=}CH_2$ with 2 equiv of *t*-BuHgI yields radical **18** (Scheme 2) which cyclizes to give the 5-exo (**19**, 9%) and 6-endo (**20**, 52%) products.

Scheme 2



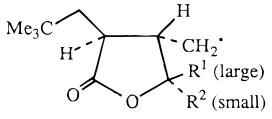
Photolysis of the mixture of cyclized organomercurials with Ph_2S_2 gives as the major products *cis*- and *trans*-6-(2,2-dimethylpropyl)-2,2-dimethyl-4-(phenylthio)cyclohexanones in a 1:1 ratio. Reaction of the starting ketone with *t*-BuHgI/NH_4I at 25 °C produces 36% of the uncyclized reductive alkylation product and 45% of the cyclized mercurials. This product ratio is similar to that observed with $CH_2{=}CHC(O)OC(Me)_2CH{=}CH_2$, indicating that adduct radicals from these alkenes

Scheme 3



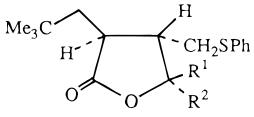
probably undergo cyclization at comparable rates. Radical **21** (Scheme 3) underwent a much faster cyclization using the same concentration of *t*-BuHgI to give exclusively the 6-exo-cyclization product **22** as a 3:1 mixture of cis and trans isomers with an initial kinetic chain length of 100 at 35 °C. Reaction of the ketone with *t*-BuHgI/NH_4I forms the cyclized mercurial in 85% yield with only 6% of the protonolysis product of the uncyclized mercurial. For the keto radicals 6-exo-cyclization of **21** is faster than 5-exo- or 6-endo-cyclization of **18** while for the ester radicals derived from **9c** and **9f**, 5-exo-cyclization is much faster than 6-exo because of the boat conformation required for 6-exo closure of α-carboalkoxy radicals. α-Keto radicals have no restriction to 6-exo closure involving a chairlike transition state and cyclization will occur readily from the s-cis conformation.[12] The *gem*-dimethyl substitution present in **21** facilitates the 6-exo-cyclization since reaction of *t*-BuHgI/KI with $CH_2{=}CHC(O)CH_2CH_2CH_2CH{=}CH_2$ forms only the uncyclized organomercurial which in turn fails to form cyclized products upon photolysis with Ph_2S_2. However, with the less reactive Et_2S_2, cyclization does occur to give a mixture of 6-exo- and 7-endo-cyclization products.

Bicyclization Reactions. Several acrylate esters capable of undergoing tandem radical cyclizations were examined. The products observed lead to the conclusion that the cyclization of **4** occurs so that the largest of the substituents R^1 and R^2 will be located trans to the carbinyl radical center, **23**. This is

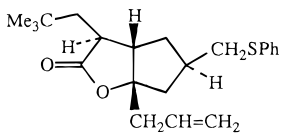


23

consistent with the geometry observed for the cyclized product **10b**. Reaction of **9g** or **9h** with Ph_2S_2 gives only the mono-cyclization products **24a** (55%) or **24b** (45%), but for **9i** a second 5-exo-cyclization occurs to yield **25** in 66% yield. With

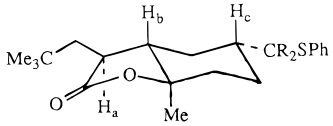


24, **a**, $R^1 = CH{=}CH_2$, $R^2 = H$
b, $R^1 = CH_2CH{=}CH_2$, $R^2 = Me$



25

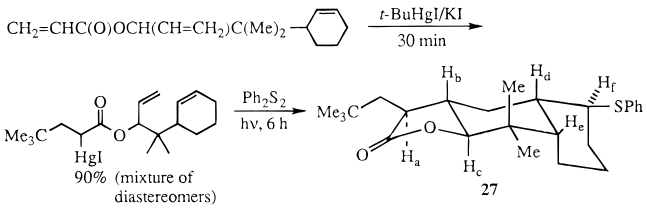
9j a mixture of products derived from competitive 5-exo- and 8-endo-cyclization is observed.[23] However, for **9k** or **9l**, the *gem*-dialkyl substitution pattern favors 5-exo- over 8-endo-cyclization; see Table 3. Photolysis of **9k** or **9l** with Ph_2S_2 thus forms **26a** or **26b** as single diastereomers in yields of 50 and 40%, respectively. The stereochemistry of **26** is controlled by



26, **a**, R = H
b, R = Me

(23) Russell, G. A.; Li, C. *Tetrahedron Lett.* **1996**, *37*, 2557.
(24) Clive, D. L. J.; Cheshire, D. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1520.
(25) Snider, B. B.; Cole, B. M. *J. Org. Chem.* **1995**, *60*, 5376.

Scheme 4



the intermediate radical **23** in which the larger homoallylic substituent is trans to the radical center. 6-Exo-cyclization then leads to a trans 5:6 ring fusion in **26** whose structure was assigned on the basis of a strong NOE between the angular methyl group and H_a but not H_b as well as strong NOE between H_b and H_c (J_{ab} for **26b** = 13.8 Hz). The trans 5:6 ring fusion with homoallyl substituents is not kinetically preferred because **23** with two homoallyl substituents gives a mixture of cis and trans bicyclization products. Another example of stereoselectivity in bicyclization is given in Scheme 4 where radical **23** with R^1 = 1-(3-cyclohexenyl)-1-methylethyl and R^2 = H leads first to a trans 5:6 and then to a cis 6:6 ring fusion. The diastereomer **27** isolated in 30% yield had J_{ab} = 12.4, J_{bc} = 11.2 Hz and displayed a strong NOE between H_a and H_c and between H_b and H_d but no NOE between H_e and H_c or H_f. In addition, H_c and H_d had strong NOE with different methyl groups while both methyls gave NOE with H_e and the equatorial proton H_f was a multiplet with the sum of coupling constants < 8 Hz.

Experimental Section

NMR spectra were recorded in $CDCl_3$ (^{1}H at 300 or 400 MHz and ^{13}C at 75.47 MHz) using TMS as an internal standard. 2D NMR spectra were obtained with a Bruker DRX400 spectrometer. EIMS (70 eV) were obtained with Finnigan 4000 (GC mode) and Kratos MS-50 spectrometers. All mp's were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Most products were isolated by TLC on silica gel with hexane (90%)−ethyl acetate (10%) as the eluent. Photostimulated reactions utilized a Sylvania 275 W fluorescent sunlamp and Pyrex reaction vessels at 35−40 °C. Yields were based on the starting dienes or enynes by ^{1}H NMR using toluene as the internal standard. Me_2SO was purchased from Aldrich Chemical Co. and stored over 4A molecular sieves. *tert*-Butylmercury halides were prepared according to literature procedures.[1] The preparation of substrates that were not commercially available is summarized in the supporting information.

Formation of Cyclized Organomercurials and/or Phenylthio Substitution Products. The diene (0.5 mmol) in 5 mL of deoxygenated Me_2SO in the presence of 1−4 mmol of *t*-BuHgX was photolyzed at 35−40 °C and the resulting product mixture added to 150 mL of ether, extracted with H_2O, dried over $MgSO_4$, and after evaporation of the solvent isolated by TLC. The cyclized orgnaomercurials were converted to the corresponding phenyl sulfides without isolation by addition of 2 equiv of Ph_2S_2 to the Me_2SO solution followed by photolysis for 5−10 h and isolation as described above.

Measurement of kinetic chain lengths. Reactions were monitored by ^{1}H NMR in Me_2SO-d_6 with toluene as an internal standard. NMR tubes (5 mm) were filled under N_2 with and without 10 mol % (*t*-Bu)$_2$NO$^\bullet$ and reactions performed under identical conditions in a parallel fashion. For typical plots used in the calculation of the initial kinetic length, see ref 1. Standard concentrations were 0.1 M substrate, 0.12 M *t*-BuHgI, and 0.3 M KI.

4-(Chloromercuriomethyl)-3-(2,2-dimethylpropyl)-1-(2-propenyl)-pyrrolidine (1d). The major (cis) isomer of **1d** isolated by TLC had the following data: MS *m/z* (relative intensity) 431.1306 (3, calcd for $C_{13}H_{24}ClHgN$ 431.1304), 416 (3), 194 (100); ^{1}H NMR δ 0.87 (s, 9 H), 1.28 (dd, J = 13.8, 9.3 Hz, 1 H), 1.46 (dd, J = 13.8, 3.3 Hz, 1 H), 1.81 (dd, J = 12.3, 4.5 Hz, 1 H), 1.92 (dt, J = 12.3, 2.1 Hz, 1 H), 2.16−2.28 (m, 1 H), 2.41−2.54 (m, 3 H), 2.60 (dd, J = 10.2, 6.9 Hz, 1 H), 2.67−2.73 (m, 1 H), 3.18−3.36 (m, 2 H), 5.07−5.21 (m, 2 H), 5.98−6.12 (m, 1 H); ^{13}C NMR δ 29.86, 30.29, 30.83, 36.18, 41.59, 45.18, 58.15, 58.37, 60.93, 117.40, 135.18. Strong NOE was observed between the methine hydrogens (δ 2.16−2.28 and 2.67−2.73) and between two of the diastereotopic hydrogen atoms of the Me_3CH_2 (δ 1.46) and $ClHgCH_2$ (δ 1.92) group, which by COSY were shown to be coupled to the methine hydrogens at δ 2.16−2.28 and 2.67−2.73, respectively. The methine hydrogens had strong NOEs with the adjacent cis methylene hydrogens at C-2 and C-4 but not with the trans methylene hydrogens, which, respectively, gave strong NOEs with the other diastereotopic hydrogens of the Me_3CCH_2 (δ 1.28) and $ClHgCH_2$ (δ 1.81) groups. Photolysis of **1d** with Ph_2S_2 formed the sulfides in a 6:1 ratio by ^{1}H NMR.

[2-(2,2-Dimethylpropyl)cyclopentyl]methyl Phenyl Sulfide. A cis−trans mixture (4:1 by ^{1}H NMR) was isolated by TLC upon photolysis of **1a** with Ph_2S_2: MS *m/z* (relative intensity) 262.1759 (61, calcd for $C_{17}H_{26}S$ 262.1755), 247 (4), 205 (46), 123 (29), 110 (66), 96 (55), 57 (100). Major isomer: ^{1}H NMR δ 0.90 (s, 9 H), 1.10 (dd, J = 13.8, 8.4 Hz, 1 H), 1.42 (dd, J = 13.8, 3.3 Hz, 1 H), 1.18−2.14 (m, 8 H), 2.62 (dd, J = 12.0, 10.8 Hz, 1 H), 3.05 (dd, J = 12.0, 4.5 Hz, 1 H), 7.11−7.34 (m, 5 H); ^{13}C NMR δ 22.19, 29.96, 30.11, 30.90, 32.16, 34.25, 39.52, 43.33, 43.63, 125.50, 128.73, 128.80, 137.55.

[4,4-Bis(carboxyethyl)-2-(2,2-dimethylpropyl)cyclopentyl]methyl Phenyl Sulfide. A 7:1 mixture of the cis and trans isomers (based on NMR) was isolated by TLC upon photolysis of **1b** with Ph_2S_2: MS *m/z* (relative intensity) 406.2178 (55, calcd for $C_{23}H_{34}O_4S$ 406.2178), 349 (25), 297 (38), 223 (42), 173 (86), 166 (100), 165 (85), 93 (43), 69 (68), 57 (83). Major isomer: ^{1}H NMR δ 0.90 (s, 9 H), 1.15 (dd, J = 13.8, 7.8 Hz, 1 H), 1.23 (t, J = 7.2 Hz, 6 H), 1.42 (dd, J = 13.8, 3.3 Hz, 1 H), 2.02 (dd, J = 12.6, 9.9 Hz, 1 H), 2.08−2.26 (m, 2 H), 2.35−2.49 (m, 3 H), 2.64 (dd, J = 12.3, 10.8 Hz, 1 H), 3.05 (dd, J = 12.3, 4.5 Hz, 1 H), 4.13−4.21 (m, 4 H), 7.14−7.35 (m, 5 H); ^{13}C NMR δ 13.95, 29.95, 30.77, 34.25, 38.01, 38.98, 40.44, 42.78, 42.89, 58.74, 61.32, 61.38, 125.90, 128.75, 129.54, 136.61, 172.72, 172.74.

The major isomer was assigned the cis structure on the basis of the NOESY spectra, which showed NOE between the diastereotopic hydrogens of the Me_3CCH_2 (δ 1.42) and $PhSCH_2$ (δ 3.05) groups and NOE between the other diastereotopic hydrogens (δ 1.15, 2.64) and the cis ring methylene hydrogens at δ 2.02 and 2.35−2.49, which in turn did not give NOE with methine hydrogen atoms.

3-(2,2-Dimethylpropyl)-4-[(phenylthio)methyl]tetrahydrofuran. The compound was isolated as a 5.5:1 mixture of cis and trans isomers (from ^{1}H NMR) after photolysis of **2c** with Ph_2S_2: MS *m/z* (relative intensity) 264.1553 (82, calcd for $C_{16}H_{24}OS$ 264.1548), 249 (10), 207 (27), 154 (26), 139 (26), 123 (41), 110 (43), 83 (31), 70 (58), 57 (100). Major isomer: ^{1}H NMR δ 0.90 (s, 9 H), 1.20 (dd, J = 13.8, 8.7 Hz, 1 H), 1.51 (dd, J = 13.8, 3.3 Hz, 1 H), 2.27−2.40 (m, 2 H), 2.72 (dd, J = 12.6, 10.8 Hz, 1 H), 3.11 (ddd, J = 12.9, 4.2, 1.2 Hz, 1 H), 3.42 (t, J = 8.4 Hz, 1 H), 3.81 (ddd, J = 8.7, 5.4, 1.2 Hz, 1 H), 3.91 (dd, J = 8.7, 3.0 Hz, 1 H), 4.00 (t, J = 8.1 Hz, 1 H), 7.16−7.36 (m, 5 H); ^{13}C NMR δ 29.82, 30.65, 32.60, 38.84, 41.48, 42.75, 71.74, 73.18, 126.09, 128.87, 129.48, 136.29. The major isomer was assigned the cis structure on the basis of the NOESY spectra, which showed strong NOEs between the methylene protons of the Me_3CCH_2 and $PhSCH_2$ substituents and between these hydrogen and methylene ring hydrogens that did not give strong NOE with the methine hydrogens.

3-(2,2-Dimethylpropyl)-4-methylenetetrahydrofuran. The mercurial **2a** was formed in an approximately 2:1 ratio of *E* and *Z* isomers (by ^{1}H NMR). Reduction by $NaBH_4$ in CH_2Cl_2 containing a trace of H_2O formed the methylene compound: ^{1}H NMR δ 0.93 (s, 9 H), 1.29 (dd, J = 14.4, 9.6 Hz, 1 H), 1.62 (dd, J = 14.4, 2.4 Hz, 1 H), 2.58−2.68 (m, 1 H), 3.39 (t, J = 8.4 Hz, 1 H), 4.18−4.26 (m, 2 H), 4.35−4.41 (m, 1 H), 4.88−4.95 (m, 2 H); ^{13}C NMR δ 29.84, 30.55, 40.46, 46.66, 71.06, 75.75, 102.75, 153.47; MS *m/z* (relative intensity) 154.1358 (5, calcd for $C_{10}H_{18}O$ 154.1358), 139 (9), 121 (4), 97 (10), 83 (24), 57 (100).

4-(2,2-Dimethylpropyl)-2,2-dimethyl-3-methylenetetrahydrofuran. The mercurial **2b** was formed as an approximately 1.7:1 mixture of *E* and *Z* isomers (by ^{1} H NMR). Reduction with $NaBH_4$ in CH_2Cl_2 containing a trace of H_2O formed the methylene compound: ^{1}H NMR δ 0.92 (s, 9 H), 1.24 (s, 3 H), 1.30 (dd, J = 14.4, 9.6 Hz, 1 H), 1.32 (s, 3 H), 1.59 (dd, J = 14.4, 2.4 Hz, 1 H), 2.68−2.79 (m, 1 H), 3.40

(t, J = 8.7 Hz, 1 H), 4.14 (t, J = 8.1 Hz, 1 H), 4.81 (t, J = 2.4 Hz, 2 H); ^{13}C NMR δ 27.30, 28.73, 29.87, 30.58, 40.82, 47.48, 71.96, 81.33, 102.47, 161.83; MS *m/z* (relative intensity) 182.1667 (1, calcd for $C_{12}H_{22}O$ 182.1671), 167 (100), 125 (3), 57 (40).

3-(2,2-Dimethylpropyl)-2-hydroxy-4-methyl-1,2-oxaphosphane 2-Oxide. The mercurial **3a** was conviently formed in benzene solution. After evaporation of the solvent the mercurial was reduced by $NaBH_4$ in CH_2Cl_2 in the presence of a trace of H_2O. Filtration and solvent removal gave an essentially pure mixture of two isomers in equal amounts: MS *m/z* (relative intensity) 207 (39), 206.1072 (12, calcd for $C_9H_{19}O_3P$ 206.1072), 191 (31), 149 (49), 109 (55), 84 (40), 57 (45), 41 (100); ^{1}H NMR δ 0.977 (s, 9 H) and 0.984 (s, 9 H), 1.040 (d, J = 6.6 Hz, 3 H) and 1.142 (d, J = 7.2 Hz, 3 H), 1.238−1.924 (m, 5 H), 2.018−2.209 (m, 2 H), 2.424−2.590 (m, 1 H), 3.603 (ddd, J = 11.1, 9.0, 2.1 Hz, 1 H) and 3.895 (ddd, J = 18.6, 9.0, 2.1 Hz, 1 H), 4.134−4.255 (m, 2 H); ^{13}C NMR δ 14.109 (d, J_{CCCP} = 2.8 Hz) and 15.369 (d, J_{CCCP} = 15.3 Hz), 29.373 and 29.394, 30.422 (d, J_{CCCP} = 1.2 Hz) and 30.750 (d, J_{CCCP} = 6.8 Hz), 32.194 (d, J_{CP} = 122.6 Hz) and 35.352 (d, J_{CP} = 124.7 Hz), 36.472 (d, J_{CCP} = 6.2 Hz) and 36.990 (d, J_{CCP} = 1.6 Hz), 39.155 (d, J_{CCP} = 8.0 Hz) and 40.800 (d, J_{CCP} = 1.8 Hz), 71.520 (d, J_{COP} = 7.9 Hz) and 72.955 (d, J_{COP} = 9.9 Hz).

Allyl 3-(2,2-Dimethylpropyl)-4-(iodomercuriomethyl)propylphostonate (3b). Three diastereomers in approximately equal amounts (by ^{1}H NMR) were isolated in pure form (see the supporting information for spectroscopic data). The structures were assigned by 2D NOESY as the 2α,3α,4α (O, Me_3CCH_2, and CH_2HgI all cis), 2α,3α,4β, and 2α,3β,4α diastereomers. Photolysis of the isomers of **3b** with Ph_2S_2 formed three isomeric phenyl sulfides of which two, formed in approximately equal amounts (by ^{1}H NMR), greatly predominated and were isolated by TLC. Allyl (2α,3α,4β)-(±)-3-(2,2-dimethylpropyl)-4-[(phenylthiomethyl]propylphostonate: ^{1}H NMR δ 0.94 (s, H), 1.20 (ddd, J_{HCCP} = 27, J = 14.4, 2.1 Hz, 1 H), 1.67−1.82 (m, 1H), 2.00 (ddd, J_{HCCP} = 20.4, J = 14.1, 9.0 Hz, 1 H), 2.30−2.43 (m, 1 H), 2.79 (ddd, J = 13.5, 9.6 Hz, J_{HCCCP} = 1.8 Hz, 1 H), 3.27 (dd, J = 13.5, 3.9 Hz, 1 H), 3.73 (ddd, J_{HCOP} = 9.6, J = 9.6, 3.3 Hz, 1 H), 4.35 (ddd, J_{HCOP} = 21, J = 9.3, 6.6 Hz, 1 H), 4.54−4.62 (m, 2 H), 5.23−5.39 (m, 2 H), 5.88−6.00 (m, 1 H), 7.23−7.37 (m, 5H); ^{13}C NMR δ 29.12, 30.61 (d, J_{CCCP} = 2.4 Hz), 33.20 (d, J_{CP} = 123 Hz), 35.73 (d, J_{CCP} = 16.3 Hz), 40.83 (d, J_{CCCP} = 1.4 Hz), 44.12 (d, J_{CCP} = 8.7 Hz), 66.77 (d, J_{COP} = 7.2 Hz), 69.30 (d, J_{COP} = 6.7 Hz), 118.2, 127.0, 129.2, 130.3, 132.85 (d, J_{CCOP} = 6.3 Hz), 134.7; MS *m/z* (relative intensity) 354.1411 (21, calcd for $C_{18}H_{27}O_3PS$ 354.1419), 294 (4), 245 (23), 149 (100), 57 (19). Strong NOE was observed between the 3-methine hydrogen and the methylene hydrogens of $PhSCH_2$ and between the 4-methine hydrogen and one of the diastereotopic methylene hydrogens of Me_3CCH_2. There was a weak NOE between the 3-methine and methylene of the allyl group. 2α,3α,4α Isomer: ^{1}H NMR δ 0.94 (s, 9 H), 1.43 (ddd, J_{HCCP} = 21.9, J = 14.4, 4.5 Hz, 1 H), 1.80 (ddd, J_{HCCP} = 18, J = 14.4, 7.6 Hz, 1 H), 2.16 (dddd, J_{HCP} = 19.2, J = 7.2, 7.2, 4.5 Hz, 1 H), 2.40−2.58 (m, 1 H), 3.01 (dd, J = 13.5, 12 Hz, 1 H), 3.21 (dd, J = 13.5, 3.5 Hz, 1 H), 4.01 (dddd, J = 9.6, 4.5, J_{HCOP} = 2.7, J_{HCCCP} = 1.5 Hz, 1 H), 4.42 (ddd, J_{HCOP} = 19.5, J = 9.7, 2.4 Hz, 1 H), 4.54−4.61 (m, 2 H), 5.22−5.38 (m, 2 H), 5.87−6.00 (m, 1 H), 7.18−7.37 (m, 5 H); ^{13}C NMR δ 29.24, 30.80 (d, J_{CCCP} = 5.4 Hz), 32.07 (d, J_{CCP} = 3.1 Hz), 32.25 (d, J_{CP} = 122 Hz), 36.78, 41.71 (d, J_{CCP} = 5.9 Hz), 66.83 (d, J_{COP} = 7.5 Hz), 118.16, 126.73, 129.09, 130.07, 132.92 (d, J_{CCOP} = 5.7 Hz), 134.95; MS *m/z* (relative intensity) 354.1212 (8, calcd for $C_{18}H_{27}O_3PS$ 354.1419), 339 (4), 313 (4), 232 (15), 245 (6), 149 (100), 109 (10), 57 (9). Among the NOEs was a strong interaction between diastereotopic hydrogens of the Me_3CH_2 and CH_2SPh substituents and between the methine hydrogens at C-3 and C-4. The 5-β methylene hydrogen had NOE with the 4-methine hydrogen and the allyl methylene but not with the $PhSCH_2$ methylene while the allyl methylene had a weak NOE with the 3-methine hydrogen.

***trans*-3-(2,2-Dimethylpropyl)-4-(iodomercuriomethyl)dihydro-2(3*H*)-furanone.** A mixture of 2-propenyl acrylate (56 mg, 0.5 mmol) and *t*-BuHgI (385 mg, 1.0 mmol) was dissolved in Me_2SO (5 mL) and the solution photolyzed for 1 h. The resulting mixture was diluted with 150 mL of ether, washed with H_2O, and dried over $MgSO_4$. After evaporation of the solvent, the mercurial was isolated in 10% yield by TLC with hexane (90%)−ethyl acetate (10%) as the eluent: ^{1}H NMR δ 0.991 (s, 9 H), 1.368 (dd, J = 3.6, 14.1 Hz, 1 H), 1.865 (dd, J = 6.0, 14.1 Hz, 1 H), 2.010−2.087 (m, 2 H), 2.249 (dd, J = 6.0, 12.0 Hz, 1 H), 2.700−2.780 (m, 1 H), 3.794 (t, J = 8.4 Hz, 1 H), 4.443 (dd, J = 6.9, 8.7 Hz, 1 H); ^{13}C NMR δ 29.75, 30.95, 42.90, 44.01, 45.34, 45.76, 72.93, 168.52; MS *m/z* (relative intensity) 497.9987 (1, calcd for $C_{10}H_{17}$-HgIO 497.9980), 441 (20), 440 (10), 439 (18), 438 (11), 169 (52), 113 (45), 57 (100).

***trans*-3-(2,2-Dimethylpropyl)-4-(iodomercuriomethyl)-5,5-dimethyldihydro-2(3*H*)-furanone (5)** was prepared following the above procedure in 65% yield from 1,1-dimethyl-2-propenyl acrylate as a colorless oil: ^{1}H NMR δ 0.940 (s, 9 H), 1.297 (s, 3 H), 1.452 (dd, J = 7.2, 12.0 Hz, 1 H), 1.485 (s, 3 H), 1.845−1.906 (m, 2 H), 1.973 (dd, J = 7.2, 12.0 Hz, 1 H), 2.137 (ddd, J = 1.6, 6.8, 12.3 Hz; 1 H), 2.277 (dt, J = 12.3, 7.2 Hz, 1 H); ^{13}C NMR δ 21.86, 27.60, 29.75, 30.90, 36.86, 42.99, 44.04, 53.16, 85.06, 177.84. The coupling constant for the trans methine hydrogens at C-3 and C-4 was 12.3 Hz.

3-(2,2-Dimethylpropyl)-5,5-dimethyl-4-[(phenylthio)methyl]-2(5*H*)-furanone. A Me_2SO (5 mL) solution of 1,1-dimethylpropynyl acrylate (69 mg, 0.5 mmol), *t*-BuHgI (289 mg, 0.75 mmol), and Ph_2S_2 (218 mg, 1.0 mmol) was photolyzed for 2 h. Workup and TLC gave the sulfide in 55% yield as a colorless liquid: ^{1}H NMR δ 0.938 (s, 9 H), 1.485 (s, 6 H), 2.153 (s, 2 H), 2.593 (s, 2 H), 7.135−7.387 (m, 5 H); ^{13}C NMR δ 26.27, 28.48, 30.23, 34.54, 37.50, 98.77, 126.50, 127.93, 129.17, 131.02, 133.51, 150.97, 156.49; HRMS 304.1498 (calcd for $C_{18}H_{24}O_2S$ 304.1497).

3-(2,2-Dimethylpropyl)-4,5,5-trimethyl-2(5H)-furanone. A Me_2-SO (5 mL) solution of 1,1-dimethylpropynyl acrylate (69 mg, 0.5 mmol) and *t*-BuHgI (385 mg, 1.0 mmol) was photolyzed for 2 h, and the resulting solution containing **6** added to 50 mL of H_2O and extracted with CH_2Cl_2. Excess $NaBH_4$ was added to the CH_2Cl_2 solution, which after 1 h at room temperature was washed with brine and dried over $MgSO_4$. After the evaporation of the solvent, the crude product was purified by TLC to give the reduction product in 50% yield as a solid: mp 55−56 °C; ^{1}H NMR δ 0.922 (s, 9 H), 1.423 (s, 6 H), 1.931 (s, 3 H), 2.136 (s, 2 H); ^{13}C NMR δ 12.06, 25.02, 29.76, 33.45, 36.66, 85.32, 126.66, 166.04, 173.76; MS *m/z* (relative intensity) 197 (2), 196.1468 (1, calcd for $C_{12}H_{20}O_2$ 196.1463), 181 (10), 140 (100), 125 (18), 95 (12), 57 (14).

***trans*-3-(2,2-Dimethylpropyl)-4,5,5-trimethyldihydro-2(3*H*)-furanone.** Photolysis of the Me_2SO (5 mL) solution of 1,1-dimethyl-2-propenyl acrylate (70 mg, 0.5 mmol) and *t*-BuHgI (385 mg, 1.0 mmol) for 1 h yielded **5** in 65% yield (by ^{1}H NMR), which was reduced by excess $NaBH_4$ in the presence of trace H_2O at room temperature for 10 min. The resulting mixture was poured into ether (150 mL), washed with brine (50 mL), and dried over anhydrous $MgSO_4$. After the evaporation of the solvent, the crude product was purified by TLC to give the product as a white solid in 55% yield: mp 70−71 °C; ^{1}H NMR δ 0.920 (s, 9 H), 1.020 (d, J = 5.1 Hz, 3 H), 1.130 (dd, J = 1.5, 10.8 Hz, 1 H), 1.225 (s, 3 H), 1.376 (s, 3 H), 1.854 (dd, J = 4.8, 10.8 Hz, 1 H), 1.889 (qd, J = 5.1, 6.3 Hz, 1 H), 2.144 (ddd, J = 1.5, 4.8, 6.3 Hz, 1 H); ^{13}C NMR δ 12.86, 21.51, 27.17, 29.46, 30.61, 42.60, 42.95, 48.12, 84.44, 178.98; MS *m/z* (relative intensity) 198.1622 (1, calcd for $C_{12}H_{22}O_2$ 198.1620), 181 (2), 131 (2), 109 (100).

***trans*-3-(2,2-Dimethylpropyl)-4-(iodomercuriomethyl)-1-phenyl-2-pyrrolidinone (7b)** was prepared from *N*-allyl-*N*-phenylacrylamide in 85% yield as a colorless oil following the procedure used for the preparation of **5**: ^{1}H NMR δ 1.004 (s, 9 H), 1.350 (dd, J = 4.8, 14.1 Hz, 1 H), 1.893 (dd, J = 4.5, 14.1 Hz, 1 H), 2.160−2.220 (m, 2 H), 2.332 (dd, J = 5.1, 12.6 Hz, 1 H), 2.680−2.743 (m, 1 H), 3.420 (dd, J = 6.6, 9.6 Hz, 1 H), 3.996 (dd, J = 6.9, 9.6 Hz, 1 H), 7.135 (t, J = 7.2 Hz, 1 H), 7.357 (dd, J = 7.2, 7.8 Hz, 2 H), 7.597 (d, J = 7.8 Hz, 2 H); ^{13}C NMR δ 29.69, 30.95, 31.39, 40.03, 41.15, 47.17, 52.03, 119.58, 124.35, 127.51, 128.79, 129.32, 133.24, 176.20; HRMS 573.0461, calcd for $C_{16}H_{22}HgINO$ 573.0453. There was no NOE between the methylene hydrogens of the Me_3CCH_2 (δ 1.350, 1.893) and the $IHgCH_2$ diastereotopic hydrogen at δ 2.332 but there was a strong NOE between this hydrogen and the 3-methine hydrogen at δ 2.680−2.743.

***trans*-3-(2,2-Dimethylpropyl)-4-(iodomercuriomethyl)-1-(2-propenyl)-2-pyrrolidinone (7c)** was prepared from *N*,*N*-diallylacrylamide according to the procedure outlined for the preparation of **5** in 85% yield as a colorless oil: ^{1}H NMR δ 0.946 (s, 9 H), 1.231 (dd, J = 6.0,

14.1 Hz, 1 H), 1.755 (dd, J = 4.2, 14.1 Hz, 1 H), 1.970 (ddd, J = 4.2, 6.0, 6.3 Hz, 1 H), 2.116 (dd, J = 7.2, 11.7 Hz, 1 H), 2.276 (dd, J = 5.1, 11.7 Hz, 1 H), 2.593−2.655 (m, 1 H), 2.860 (dd, J = 5.4, 9.6 Hz, 1 H), 3.483 (dd, J = 6.9, 9.6 Hz, 1 H), 3.850 (d, J = 5.7 Hz, 2 H), 5.136−5.196 (m, 2 H), 5.652−5.784 (m, 1 H); ^{13}C NMR δ 29.91, 31.06, 40.53, 44.10, 45.46, 45.54, 48.97, 53.53, 118.67, 132.40, 176.56; MS *m/z* (relative intensity) 539 (0.2), 538 (0.7), 537.0456 (0.8, calcd for $C_{13}H_{22}HgINO$ 537.0452), 536 (1), 535 (1), 534 (0.8), 533 (0.4), 208 (100), 152 (36), 57 (50). The structure was assigned on the basis of HETCOR and NOESY spectra, which showed only a small NOE between the 3-methine (δ 1.970) and 4-methine (δ 2.593−2.655) hydrogens but a strong NOE between the 3-methine and the *cis*-5-methylene hydrogen at δ 2.860. There was no NOE between the 3-methine hydrogen and the *trans*-5-methylene hydrogen (δ 3.483), which had a strong NOE with the 4-methine hydrogen. Only a weak NOE was observed between the 4-methine hydrogen and the 5-methylene hydrogen at δ 2.860.

***trans*-3-(2,2-Dimethylpropyl)-4-methyl-1-(2-propenyl)-2-pyrrolidinone (8a, R = 2-propenyl).** A mixture of *N*,*N*-diallylacrylamide (75.5 mg, 0.5 mmol), *t*-BuHgCl (565 mg, 2.0 mmol), and Et_3SiH (0.32 mL, 2.0 mmol) was dissolved in Me_2SO (5 mL), and the solution was kept in the dark at room temperature for 2 h. The resulting mixture was poured into ether (150 mL), washed with brine (50 mL), and dried over anhydrous $MgSO_4$. After the evaporation of the solvent, the crude product was purified by TLC to give **8a** in 90% yield as a colorless liquid: ^{1}H NMR δ 0.955 (s, 9 H), 1.123 (d, J = 6.3 Hz, 3 H), 1.183 (dd, J = 5.4, 14.1 Hz, 1 H), 1.807 (dd, J = 4.2, 14.1 Hz, 1 H), 1.965 (ddd, J = 4.2, 5.4, 6.9 Hz, 1 H), 1.982−2.100 (m, 1 H), 2.854 (dd, J = 6.0, 9.6 Hz, 1 H), 3.379 (dd, J = 7.2, 9.6 Hz, 1 H), 3.850−3.880 (m, 2 H), 5.132−5.190 (m, 2 H), 5.647−5.779 (m, 1 H); ^{13}C NMR δ 18.70, 29.75, 30.86, 35.24, 44.36, 45.33, 46.77, 52.24, 117.66, 132.76, 177.39; MS *m/z* (relative intensity) 209.1783 (33, calcd for $C_{13}H_{23}NO$ 209.1780), 194 (64), 152 (100), 138 (82), 70 (45).

***trans*-3-(2,2-Dimethylpropyl)-4-[(phenylthio)methyl]-1-(2-propenyl)-2-pyrrolidinone (8b, R = 2-propenyl).** A mixture of *N*,*N*-diallylacrylamide (0.5 mmol), *t*-BuHgI (0.6 mmol), and KI (1.5 mmol) in 5 mL of Me_2SO in the dark at room temperature showed by ^{1}H NMR that all the acrylamide had been consumed in 30 min. Ph_2S_2 (218 mg, 1 mmol) was added and the mixture photolyzed for 8 h. The resulting solution was added to H_2O and extracted with ether and the extract dried over $MgSO_4$. The solvent was evaporated and the product purified by TLC to give **8b** in 80% yield as a colorless oil: ^{1}H NMR δ 0.914 (s, 9 H), 1.191 (dd, J = 6.0, 13.8 Hz, 1 H), 1.765 (dd, J = 3.0, 13.8 Hz, 1 H), 2.199 (ddd, J = 3.0, 4.8, 6.0 Hz, 1 H), 2.510−2.550 (m, 1 H), 2.814 (dd, J = 9.9, 13.2 Hz, 1 H), 3.176 (dd, J = 4.8, 9.9 Hz, 1 H), 3.212 (dd, J = 3.6, 13.2 Hz, 1 H), 3.440 (dd, J = 4.8, 10.2 Hz, 1 H), 3.850−3.870 (m, 2 H), 5.134−5.193 (m, 2 H), 5.626−5.756 (m, 1 H), 7.185−7.355 (m, 5 H); ^{13}C NMR δ 29.70, 30.95, 38.07, 39.45, 44.48, 45.16, 45.38, 49.64, 118.09, 126.62, 129.07, 129.95, 130.36, 132.38, 135.42, 176.50; MS *m/z* (relative intensity) 317.1808 (100, calcd for $C_{19}H_{27}NOS$ 317.1813), 302 (46), 260 (53), 208 (73), 194 (80), 150 (57), 123 (41), 69 (53), 41 (65).

***trans*-3-(2,2-Dimethylpropyl)-1-phenyl-4-[(phenylthio)methyl]-2-pyrrolidinone (8b, R = phenyl)** was prepared from *N*-allyl-*N*-phenylacrylamide according to the above procedure as a colorless oil: ^{1}H NMR δ 0.949 (s, 9 H), 1.274 (dd, J = 5.7, 14.1 Hz, 1 H), 1.869 (dd, J = 3.9, 14.1 Hz, 1 H), 2.256−2.391 (m, 2 H), 2.892 (dd, J = 9.9, 13.2 Hz, 1 H), 3.293 (dd, J = 4.2, 13.2 Hz, 1 H), 3.672 (dd, J = 5.7, 10.2 Hz, 1 H), 3.927 (dd, J = 6.9, 10.2 Hz, 1 H), 7.098−7.387 (m, 8 H), 7.589−7.629 (m, 2 H); ^{13}C NMR δ 29.67, 30.97, 37.61, 39.18, 44.24, 46.33, 51.24, 119.58, 124.38, 126.74, 128.80, 129.15, 130.02, 135.21, 139.44, 176.08; MS *m/z* (relative intensity) 353.1805 (75, calcd for $C_{22}H_{27}NOS$ 353.1813), 338 (24), 296 (21), 244 (100), 230 (63), 186 (32), 137 (40), 106 (85), 77 (41), 57 (81). The structure was confirmed by 2D COSY and NOESY.

***trans*-3-(2,2-Dimethylpropyl)-1-methyl-4-[(phenylthio)methyl]-2-pyrrolidinone (8b, R = Me)** was prepared in 90% yield as a colorless oil from *N*-allyl-*N*-methylacrylamide according to the above procedure: ^{1}H NMR δ 0.905 (s, 9 H), 1.171 (dd, J = 6.3, 14.1 Hz, 1 H), 1.752 (dd, J = 3.6, 14.1 Hz, 1 H), 2.116−2.239 (m, 2 H), 2.809 (t, J = 11.4 Hz, 1 H), 2.816 (s, 3 H), 3.182−3.247 (m, 2 H), 3.463 (dd, J = 7.2, 9.9 Hz, 1 H), 7.187−7.364 (m, 5 H); ^{13}C NMR δ 29.76, 29.92, 31.00, 38.14, 39.46, 44.58, 45.00, 52.39, 126.70, 129.15, 130.02, 135.48, 176.88; HRMS calcd for $C_{17}H_{23}NO$ 257.1780, found 257.1781. The structure was confirmed by 2D COSY and NOESY.

***trans*-3-(2,2-Dimethylpropyl)-4-[(phenylseleno)methyl]-1-(2-propenyl)-2-pyrrolidinone (8c, R = 2-propenyl).** Photolysis of *N*,*N*-diallylacrylamide (75.5 mg, 0.5 mmol) and *t*-BuHgI (385 mg, 1.0 mmol), in Me_2SO (5 mL) for 1 h was followed by the addition of Ph_2Se_2 (312 mg, 1.0 mmol) and the solution was further photolyzed for 2 h. The resulting mixture was poured into ether (150 mL), washed with brine (50 mL), and dried over anhydrous $MgSO_4$. After the evaporation of the solvent, the crude product was purified by TLC to give the product in 80% yield as a colorless oil: ^{1}H NMR δ 0.894 (s, 9 H), 1.158 (dd, J = 6.0, 14.1 Hz, 1 H), 1.751 (dd, J = 3.9, 14.1, 1 H), 2.119−2.230 (m, 2 H), 2.796 (dd, J = 9.9, 12.3 Hz, 1 H), 3.115 (dd, J = 4.8, 10.2, 1 H), 3.196 (dd, J = 3.9, 12.3 Hz, 1 H), 3.438 (dd, J = 7.2, 10.2 Hz, 1 H), 3.831−3.856 (2 H, m, 2 h), 5.112−5.182 (m, 2 H), 5.598−5.744 (m, 1 H), 7.255−7.276 (m, 3 H), 7.479−7.510 (m, 2 H); ^{13}C NMR δ 29.68, 30.91, 32.00, 40.26, 44.39, 45.35, 45.99, 50.40, 118.03, 127.37, 129.21, 132.36, 133.16, 133.50, 176.56; MS *m/z* (relative intensity) 365.1265 (20, calcd for $C_{19}H_{27}NOSe$ 365.1258), 308 (29), 208 (50), 150 (36), 70 (93), 41 (100).

***trans*-3-(2,2-Dimethylpropyl)-1-phenyl-4-[(phenylseleno)methyl]-2-pyrrolidinone (8c, R = phenyl)** was prepared from *N*-allyl-*N*-phenylacrylamide using the above procedure in 80% yield as a colorless oil: ^{1}H NMR δ 0.931 (s, 9 H), 1.232 (dd, J = 5.4, 13.8, 1 H), 1.856 (dd, J = 3.6, 13.8 Hz, 1 H), 2.261−2.354 (m, 2 H), 2.872 (dd, J = 9.6, 12.6 Hz, 1 H), 3.271 (dd, J = 3.9, 12.6 Hz, 1 H), 3.611 (dd, J = 6.0, 10.2 Hz, 1 H), 3.922 (dd, J = 6.9, 10.2 Hz, 1 H), 7.095−7.604 (m, 10 H); ^{13}C NMR δ 29.70, 30.96, 31.40, 40.04, 44.16, 47.18, 52.04, 119.58, 124.36, 127.52, 128.80, 129.32, 133.24, 133.42, 134.43, 139.47, 176.20; MS *m/z* (relative intensity) 401.1257 (8, calcd for $C_{22}H_{27}NOS$ 401.1258), 344 (7), 244 (34), 160 (25), 77 (33), 57 (60), 41 (100).

***trans*-3-(2,2-Dimethylpropyl)-4-(iodomethyl)-1-(2-propenyl)-2-pyrrolidinone (8d, R = 2-propenyl).** Photolysis of *N*,*N*-diallylacrylamide (75.5 mg, 0.5 mmol) and *t*-BuHgI (385 mg, 1.0 mmol) in Me_2SO (5 mL) for 1 h was followed by the addition of I_2 (254 mg, 1.0 mmol), and the solution was kept in the dark at room temperature for 12 h. The resulting mixture was poured into ether (150 mL), washed with H_2O (50 mL), and dried over anhydrous $MgSO_4$. After the evaporation of the solvent, the crude product was purified by TLC to give the product in 80% yield as a colorless oil: ^{1}H NMR δ 0.972 (s, 9 H), 1.210 (dd, J = 5.4, 14.4 Hz, 1 H), 1.875 (dd, J = 4.2, 14.4 Hz, 1 H), 2.129 (ddd, J = 5.4, 4.2, 7.2 Hz, 1 H), 2.175−2.274 (m, 1 H), 3.054 (dd, J = 6.3, 10.2 Hz, 1 H), 3.170 (dd, J = 9.3, 9.6 Hz, 1 H), 3.391−3.468 (m, 2 H), 3.816−3.955 (m, 2 H), 5.164−5.236 (m, 2 H), 5.654−5.786 (m, 1 H); ^{13}C NMR δ 9.28, 29.65, 30.87, 42.42, 42.36, 45.29, 45.75, 51.55, 118.10, 132.16, 175.98; MS *m/z* (relative intensity) 335.0752 (4, calcd for $C_{13}H_{22}INO$ 335.0746), 320 (20), 278 (63), 208 (100), 152 (21), 57 (37).

***trans*-3-(2,2-Dimethylpropyl)-4-(iodomethyl)-1-phenyl-2-pyrrolidinone (8d, R = phenyl)** was prepared from *N*-allyl-*N*-phenylacrylamide using the above procedure in 80% yield as a colorless oil: ^{1}H NMR δ 0.997 (s, 9 H), 1.288 (dd, J = 4.2, 14.1 Hz, 1 H), 1.978 (dd, J = 4.2, 14.1 Hz, 1 H), 2.261−2.356 (m, 2 H), 3.223 (dd, J = 9.0, 9.9 Hz, 1 H), 3.481 (dd, J = 3.6, 9.9 Hz, 1 H), 3.568 (dd, J = 6.9, 9.9 Hz, 1 H), 3.919 (dd, J = 6.9, 9.9 Hz, 1 H), 7.138 (t, J = 7.2 Hz, 1 H), 7.334−7.387 (m, 2 H), 7.628 (d, J = 8.1 Hz, 2 H); ^{13}C NMR δ 8.41, 29.72, 30.98, 42.11, 44.21, 46.91, 53.28, 119.67, 124.52, 128.82, 139.21, 175.66; MS *m/z* (relative intensity) 371.0743 (16, calcd for $C_{16}H_{22}INO$ 371.0746), 314 (31), 244 (100), 188 (19), 106 (66), 84 (30), 57 (40).

***trans*-4-(3-Butenyl)-3-(2,2-dimethylpropyl)-1-(2-propenyl)-2-pyrrolidinone (8e, R = 2-propenyl).** Photolysis of *N*,*N*-diallylacrylamide (75.5 mg, 0.5 mmol) and *t*-BuHgI (385 mg, 1.0 mmol) in Me_2SO (5 mL) for 1 h was followed by the addition of allyl phenyl sulfide (150 mg, 1.0 mmol) and the solution photolyzed for 4 h. The resulting mixture was poured into ether (150 mL), washed with brine (50 mL), and dried over anhydrous $MgSO_4$. After the evaporation of the solvent, the crude product was purified by TLC to give the product in 80% yield as a colorless liquid: ^{1}H NMR δ 0.954 (s, 9 H), 1.192 (dd, J = 5.1, 13.8 Hz, 1 H), 1.353−1.479 (m, 1 H), 1.727−2.230 (m, 6 H), 2.921 (dd, J = 6.0, 9.6 Hz, 1 H), 3.376 (dd, J = 7.2, 9.6 Hz, 1 H),

3.855−3.875 (m, 2 H), 4.966−5.058 (m, 2 H), 5.137−5.195 (m, 2 H), 5.647−5.856 (m, 2 H); ^{13}C NMR δ 29.81, 30.93, 31.46, 32.93, 39.83, 44.52, 45.33, 45.41, 50.40, 115.18, 117.76, 132.73, 137.86, 177.28. MS *m/z* (relative intensity) 249.2090 (7, calcd for $C_{16}H_{27}NO$ 249.2091), 234 (23), 192 (100), 178 (32), 109 (20), 70 (23).

***trans*-4-(3-Butenyl)-3-(2,2-dimethylpropyl)-1-phenyl-2-pyrrolidinone (8e, R = phenyl)** was prepared from *N*-allyl-*N*-phenylacrylamide using the above procedure in 80% yield as a colorless oil: ^{1}H NMR δ 0.982 (s, 9 H), 1.173−1.314 (m, 2 H), 1.446−1.581 (m, 1 H), 1.769−1.954 (m, 2 H), 2.017−2.255 (m, 3 H), 3.444 (dd, J = 6.9, 9.6 Hz, 1 H), 3.870 (dd, J = 7.2, 9.6 Hz, 1 H), 4.960−5.098 (m, 2 H), 5.722−5.862 (m, 1 H), 7.093−7.146 (m, 1 H), 7.350 (dd, J = 7.5, 8.4 Hz, 2 H), 7.629 (dd, J = 1.2, 8.4 Hz, 2 H); ^{13}C NMR δ 29.79, 30.97, 31.47, 32.50, 39.48, 44.19, 46.64, 52.08, 115.44, 119.61, 124.22, 128.79, 137.74, 139.77, 176.95; MS *m/z* (relative intensity) 285.2092 (40, calcd for $C_{19}H_{27}NO$ 285.2093), 270 (23), 245 (47), 228 (77), 214 (27), 188 (100), 174 (35), 106 (100).

***trans*-3-(2,2-Dimethylpropyl)-4-[(phenylthio)methyl]dihydro-2(3*H*)-furanone (10a).** A mixture of 2-propenyl acrylate (56 mg, 0.5 mmol), *t*-BuHgI (232 mg, 0.6 mmol), and KI (249 mg, 1.5 mmol) was dissolved in Me_2SO (5 mL) and the solution kept in the dark at room temperature for 30 min, during which time the starting acrylate was completely consumed (by ^{1}H NMR) to yield the organomercurial **9a**. Diphenyl disulfide (218 mg, 1.0 mmol) was added, and the solution was photolyzed for 8 h. The resulting mixture was poured into ether (150 mL), washed with brine (3 × 20 mL), and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude product was purified by TLC to afford **10a** as colorless oil in 65% yield: ^{1}H NMR δ 0.932 (s, 9 H), 1.288 (dd, J = 5.1, 14.1 Hz, 1 H), 1.780 (dd, J = 5.1, 14.1 Hz, 1 H), 2.303 (td, J = 5.1, 7.5 Hz, 1 H), 2.375−2.460 (m, 1 H), 2.875 (dd, J = 6.3, 13.2 Hz, 1 H), 3.223 (dd, J = 4.5, 13.2 Hz, 1 H), 4.069 (dd, J = 6.3, 9.3 Hz, 1 H), 4.372 (dd, J = 6.6, 9.3 Hz, 1 H), 7.207−7.382 (m, 5 H); ^{13}C NMR δ 29.43, 30.94, 36.46, 41.97, 42.99, 43.47, 70.31, 127.01, 129.23, 130.21, 130.70, 134.76, 179.63; HRMS calcd for $C_{16}H_{22}O_2S$ 278.1341, found 278.1342. The structure was confirmed by 2D NOESY.

(3α,4*β*,5α)-(±)-3-(2,2-Dimethylpropyl)-5-methyl-4-[(phenylthio)methyl]dihydro-2(3*H*)-furanone (10b). The product was prepared from 1-methyl-2-propenyl acrylate according to the above procedure in 50% yield as a colorless liquid: ^{1}H NMR δ 0.867 (s, 9 H), 1.178 (dd, J = 3.9, 14.4 Hz, 1 H), 1.340 (d, J = 6.3 Hz, 3 H), 1.825 (dd, J = 5.7, 14.4 Hz, 1 H), 1.914−2.011 (m, 1 H), 2.340−2.420 (m, 1 H), 2.896 (dd, J = 7.5, 13.2 Hz, 1 H), 3.177 (dd, J = 3.9, 13.2 Hz, 1 H), 4.332 (dq, J = 6.3, 7.2 Hz, 1 H), 7.138−7.305 (m, 5 H); ^{13}C NMR δ 20.68, 29.47, 30.88, 35.48, 42.28, 44.28, 50.00, 78.64, 126.93, 129.23, 130.09, 135.28, 178.81; MS *m/z* (relative intensity) 292.1497 (100, calcd for $C_{17}H_{26}O_2S$ 292.1497), 247 (57), 183 (8), 123 (55), 98 (32), 57 (46), 41 (28). The structure was confirmed by NOESY, which showed strong NOE between the 3- and 5-methine hydrogens and between 4-methine hydrogen and the 5-methyl group.

***trans*-3-(2,2-Dimethylpropyl)-5,5-dimethyl-4-[(phenylthio)methyl]-dihydro-2(3*H*)-furanone (10c)** was prepared from 1,1-dimethyl-2-propenyl acrylate according to the above procedure in 55% yield as a colorless oil: ^{1}H NMR δ 0.959 (s, 9 H), 1.209 (dd, J = 1.5, 14.1 Hz, 1 H), 1.391 (s, 3 H), 1.564 (s, 3 H), 1.874 (dd, J = 6.6, 14.1 Hz, 1 H), 2.123 (ddd, J = 3.9, 10.2, 12.3 Hz, 1 H), 2.301 (ddd, J = 1.5, 6.6, 12.3 Hz, 1 H), 2.868 (dd, J = 10.2, 12.9 Hz, 1 H), 3.221 (dd, J = 3.9, 12.9 Hz, 1 H), 7.221−7.338 (m, 5 H); ^{13}C NMR δ 21.61, 29.24, 29.50, 30.72, 33.36, 41.95, 42.91, 51.37, 84.03, 126.79, 129.25, 129.56, 135.37, 177.45; MS *m/z* 306.1655 (10, calcd for $C_{18}H_{26}O_2S$ 306.1654), 247 (28), 183 (20), 141 (41), 123 (22), 70 (50), 57 (100), 41 (47). The coupling constant for the two methine protons is 12.3 Hz. The structure was confirmed by 2D NOESY, which showed strong NOEs between the 3-methine hydrogen and one 5-methyl group and between the 4-methine hydrogen and the other 5-methyl group.

***trans*-3-[2,2-Dimethyl-3-(phenylthio)propyl]-4,5,5-trimethyldihydro-2(3*H*)-furanone (11)** was isolated in the above reaction in 16% yield as a colorless oil: ^{1}H NMR δ 1.057 (s, 3 H), 1.061 (d, J = 6.9 Hz, 3 H), 1.078 (s, 3 H), 1.242 (s, 3 H), 1.402 (s, 3 H), 1.435 (dd, J = 2.1, 14.7 Hz, 1 H), 1.876−1.986 (m, 2 H), 2.219 (ddd, J = 2.1, 6.6, 12.6 Hz, 1 H), 2.966 (AB, J = 16.5 Hz, 2 H), 7.118−7.175 (m, 1 H), 7.236−7.286 (m, 2 H), 7.332−7.363 (m, 2 H); ^{13}C NMR δ 12.90, 21.58, 26.64, 26.79, 27.19, 35.14, 40.88, 42.42, 47.23, 48.09, 84.65, 125.72, 128.92, 129.05, 138.09, 178.56; EI-MS *m/z* 306.1648 (58, calcd for $C_{18}H_{26}O_2S$ 306.1654), 197 (20), 141 (100), 113 (42), 69 (37), 55 (50). The coupling constant for the 3- and 4-methine hydrogen atoms was 12.6 Hz. The structure was confirmed by 2D COSY and NOESY.

(3α,4*β*,6α)-(±)-3-(2,2-Dimethylpropyl)-6-methyl-4-[(phenylthio)methyl]tetrahydro-2*H*-pyran-2-one (12b) was prepared from 1-methyl-3-butenyl acrylate according to the procedure outlined for the preparation of **10a** to afford **12b** in 25% yield as a colorless liquid: ^{1}H NMR δ 0.878 (s, 9 H), 1.093 (dd, J = 2.7, 14.1 Hz, 1 H), 1.380 (d, J = 6.3 Hz, 3 H), 1.630−1.715 (m, 1 H), 2.088 (dd, J = 7.2, 14.1 Hz, 1 H), 2.160−2.283 (m, 2 H), 2.398 (t, J = 11.7 Hz, 1 H), 2.638−2.688 (m, 1 H), 3.162 (dd, J = 2.4, 11.7 Hz, 1 H), 4.480−4.570 (m, 1 H), 7.187−7.320 (m, 5 H); ^{13}C NMR δ 21.09, 29.32, 30.78, 35.43, 35.98, 37.68, 38.76, 39.55, 73.31, 126.61, 129.06, 129.96, 135.40, 174.88; MS *m/z* (relative intensity) 306.1651 (68, calcd for $C_{18}H_{26}O_2S$ 306.1654), 249 (94), 177 (23), 123 (100), 110 (24), 69 (36), 57 (73). The structure was confirmed by 2D NOESY, which showed strong NOE for the 3- and 6-methine hydrogens and little NOE between the 3- and 4-methines.

(3α,4*β*,5*β*,6α)-(±)-3-(2,2-Dimethylpropyl)-tetrahydro-5,6-dimethyl-4-[(phenylthio)methyl]-2*H*-pyran-2-one (16) was prepared from **14** according to the procedure outlined for the preparation of **10a** to afford **16** in 50% yield as a colorless liquid: ^{1}H NMR δ 0.791 (s, 9 H), 0.920 (dd, J = 3.3, 13.8 Hz, 1 H), 0.986 (d, J = 6.6 Hz, 3 H), 1.316 (d, J = 6.3 Hz, 3 H), 1.666 (dddd, J = 2.4, 2.7, 6.3, 12.6 Hz, 1 H), 1.852 (ddq, J = 2.4, 6.6, 10.2 Hz, 1 H), 2.100 (dd, J = 6.0, 13.8 Hz, 1 H), 2.324 (t, J = 12.6 Hz, 1 H), 2.566 (ddd, J = 3.3, 6.0, 6.3 Hz, 1 H), 3.070 (dd, J = 2.7, 12.6 Hz, 1 H), 3.995 (dq, J = 10.2, 6.3 Hz, 1 H), 7.133−7.279 (m, 5 H); ^{13}C NMR δ 18.82, 19.74, 29.22, 30.84, 37.13, 37.36, 39.52, 40.31, 45.39, 78.69, 126.59, 129.07, 129.92, 135.56, 175.10; MS *m/z* 320.1810 (7, calcd for $C_{19}H_{28}O_2S$ 320.1810), 263 (16), 191 (10), 145 (7), 83 (20), 57 (100). The structure was confirmed by 2D NOESY, which showed strong NOE between the 3- and 6-methine hydrogen atoms and a coupling constant between the 4- and 5-methine hydrogens of 2.4 Hz.

(3α,4*β*,4aα,8a*β*)-(±)-3-(2,2-Dimethylpropyl)-4-[(phenylthio)methyl]-octahydro-2*H*-1-benzopyran-2-one (17) was prepared from **15** according to the procedure outlined for the preparation of **10a** to afford **17** in 53% yield as a white solid: mp 86−88 °C; ^{1}H NMR δ 0.880 (s, 9 H), 1.092 (dd, J = 2.4, 14.1 Hz, 1 H), 1.216−1.339 (m, 3 H), 1.410−1.590 (m, 2 H), 1.680−1.720 (m, 1 H), 1.830−1.905 (m, 2 H), 2.010−2.045 (m, 1 H), 2.110−2.165 (m, 2 H), 2.478 (dd, J = 11.7, 12.0 Hz, 1 H), 2.760 (ddd, J = 2.4, 6.9, 7.5 Hz, 1 H), 3.207 (dd, J = 3.0, 12.0 Hz, 1 H), 4.045 (ddd, J = 3.6, 10.2, 10.8 Hz, 1 H), 7.180−7.296 (m, 5 H); ^{13}C NMR δ 24.14, 25.52, 29.32, 30.85, 31.83, 32.32, 37.66, 38.37, 39.22, 42.72, 46.71, 79.53, 126.32, 129.05, 129.34, 136.07, 175.11; MS *m/z* (relative intensity) 346.1967 (30, calcd for $C_{27}H_{30}O_2S$ 346.1967), 289 (43), 217 (100), 123 (75), 57 (80), 41 (67). The structure was confirmed by 2D COSY and NOESY which showed strong NOE for the 3- and 8a-methine hydrogens but no NOE between the 4- and 8a-methines.

***cis*-6-(2,2-Dimethylpropyl)-4-(iodomercurio)-2,2-dimethylcyclohexanone (20)** was prepared from 1,1-dimethyl-3-butenyl vinyl ketone according to the general procedure outlined for the preparation of **5** to afford **20** in 52% yield as a colorless oil: ^{1}H NMR δ 0.700 (dd, J = 3.0, 14.1 Hz, 1 H), 0.817 (s, 9 H), 1.070 (s, 3 H), 1.242 (s, 3 H), 1.841 (q, J = 12.9 Hz, 1 H), 2.015 (t, J = 13.5 Hz, 1H), 2.191−2.295 (m, 2H), 2.441−2.523 (m, 1 H), 2.544−2.633 (m, 1 H), 3.129−3.245 (m, 1 H); ^{13}C NMR δ 24.70, 25.74, 29.51, 29.87, 30.65, 41.01, 44.65, 45.54, 48.28, 48.56, 214.39; HRMS 524.0510 (calcd for $C_{13}H_{23}HgIO$ 524.0500). The structure was confirmed by NOESY, which showed strong NOE between the 4- and 6-methine hydrogen atoms.

6-(2,2-Dimethylpropyl)-2,2-dimethyl-5-[(phenylthio)methyl]cyclohexanone was prepared from 1,1-dimethyl-4-pentenyl vinyl ketone via mercurial **22** according to the general procedure outlined for the preparation of **10a** to afford the cis and trans sulfides, which were separated by TLC. Trans isomer: mp 89−90 °C; ^{1}H NMR δ 0.810 (s, 9 H), 0.962 (dd, J = 0.9, 14.1 Hz, 1 H), 1.051 (s, 3 H), 1.222 (s, 3 H), 1.436−1.844 (m, 4 H), 1.954−2.043 (m, 1 H), 2.198 (dd, J = 7.8, 14.1 Hz, 1 H), 2.481 (ddd, J = 0.9, 7.8, 10.8 Hz, 1 H), 2.796 (dd, J = 9.0, 12.9 Hz, 1 H), 3.288 (dd, J = 3.0, 12.9 Hz, 1 H), 7.150−7.338

(m, 5 H); ^{13}C NMR δ 24.65, 25.54, 26.76, 29.61, 30.70, 37.53, 39.25, 39.38, 44.80, 45.13, 46.48, 126.13, 129.04, 129.28, 136.85, 215.37; MS *m/z* (relative intensity) 319 (100), 318.2025 (1, calcd for $C_{20}H_{30}OS$ 318.2017), 261 (43), 209 (16), 195 (11), 162 (29), 109 (12), 95 (12), 57 (12). The coupling constant between the 5- and 6-methine hydrogens was 10.8 Hz. The structure was confirmed by NOESY, which showed strong NOEs between the 6-methine and CH_2SPh methylene protons. The cis isomer was isolated as a colorless liquid: ^{1}H NMR δ 0.729 (dd, J = 1.8, 13.5 Hz, 1 H), 0.780 (s, 9 H), 1.041 (s, 3 H), 1.258 (s, 3 H), 1.629−1.709 (m, 2 H), 1.989−2.069 (m, 2 H), 2.180−2.289 (m, 2 H), 2.395 (t, J = 12.6 Hz, 1 H), 2.921 (dd, J = 3.0, 12.6 Hz, 1 H), 2.993 (ddd, J = 1.8, 4.8, 7.8 Hz, 1 H), 7.140−7.319 (m, 5 H); ^{13}C NMR δ 24.57, 25.32, 25.65, 29.34, 30.75, 31.44, 36.99, 39.21, 45.49, 45.79, 46.01, 126.18, 128.97, 129.49, 136.39, 215.24; MS *m/z* (relative intensity) 319 (58), 318.2026 (1, calcd for $C_{20}H_{30}OS$ 318.2017), 261 (13), 209 (28), 195 (37), 124 (100), 109 (29), 95 (47), 57 (34). The coupling constant between the 5- and 6-methine hydrogens was 4.8 Hz. The structure was confirmed by 2D NOESY, which showed no NOE between the 6-methine and CH_2SPh hydrogens.

(3α,4*β*,5α)-(±)-3-(2,2-Dimethylpropyl)-5-ethenyl-4-[(phenylthio)-methyl]dihydro-2(3*H*)-furanone (24a) was prepared from 1-vinyl-2-propenyl acrylate according to the procedure outlined for the preparation of **10a** to afford **24a** in 55% yield as colorless liquid: ^{1}H NMR δ 0.932 (s, 9 H), 1.283 (dd, J = 4.2, 14.1 Hz, 1 H), 1.854 (dd, J = 5.4, 14.1 Hz, 1 H), 2.154−2.230 (m, 1 H), 2.542 (ddd, J = 4.2, 5.4, 9.0 Hz, 1 H), 3.049 (dd, J = 6.6, 13.5 Hz, 1 H), 3.187 (dd, J = 4.2, 13.5 Hz, 1 H), 4.747 (dd, J = 6.3, 7.2 Hz, 1 H), 5.152−5.291 (m, 2 H), 5.732−5.845 (m, 1 H), 7.211−7.392 (m, 5 H); ^{13}C NMR δ 29.52, 31.00, 35.38, 41.46, 44.40, 48.97, 81.73, 118.75, 127.12, 129.29, 130.60, 135.11, 135.36, 175.98; MS *m/z* (relative intensity) 307 (3), 291.2322 [7, calcd for $C_{17}H_{21}O_2S$ (M − CH_3) 291.2324], 265 (45), 209 (23), 166 (27), 123 (51), 109 (52), 57 (100), 41 (63).

(3α,4*β*,5α)-(±)-3-(2,2-Dimethylpropyl)-5-methyl-4-[(phenylthio)-methyl]-5-(2-propenyl)dihydro-2(3*H*)-furanone (24b) was prepared from 1-methyl-1-vinyl-3-butenyl acrylate according to the procedure outlined for the preparation of **10a** to afford **24b** in 45% yield as a colorless oil: ^{1}H NMR δ 0.892 (s, 9 H), 1.164−1.211 (m, 1 H), 1.769−1.839 (m, 1 H), 2.216−2.248 (m, 2 H), 2.420 (dd, J = 7.8, 14.4 Hz, 1 H), 2.622 (dd, J = 6.9, 14.4 Hz, 1 H), 2.792−2.869 (m, 1 H), 3.123−3.178 (m, 1 H), 4.930−5.072 (m, 2 H), 5.622−5.761 (m, 1 H), 7.145−7.264 (m, 5 H); ^{13}C NMR δ 20.59, 29.55, 30.77, 33.36, 41.74, 42.99, 45.29, 47.92, 85.21, 120.04, 126.71, 129.28, 131.01, 132.12, 135.56, 177.42; MS *m/z* (relative intensity) 332.1804 (10, calcd for $C_{20}H_{28}O_2S$ 332.1810), 291 (7), 247 (13), 149 (8), 123 (91), 95 (32), 71 (22), 57 (100). The structure was confirmed by 2D NOESY, which showed strong NOEs between the 5-methyl and both the 3-methine and 4-CH_2-SPh hydrogens.

(3α,3aα,5α,6aα)-(±)-3-(2,2-Dimethylpropyl)-5-[(phenylthio)methyl]-6a-(2-propenyl)hexahydro-2*H*-cyclopenta[b]furan-2-one (25) was prepared from 1-allyl-1-vinyl-3-butenyl acrylate according to the procedure outlined for the preparation of **10a** to afford **25** in 66% yield as a colorless oil: ^{1}H NMR δ 0.890 (s, 9 H), 1.280−1.394 (m, 1 H), 1.473−1.640 (m, 1 H), 1.785 (dd, J = 1.8, 13.8 Hz, 1 H), 2.120−2.478 (m, 8 H), 2.799−2.951 (m, 2 H), 5.039−5.131 (m, 2 H), 5.611−5.736 (m, 1 H), 7.116−7.271 (m, 5 H); ^{13}C NMR δ 29.74, 31.29, 37.43, 38.09, 40.52, 43.97, 44.56, 46.38, 47.44, 49.43, 94.71, 119.79, 126.30, 129.01, 129.42, 132.39, 136.34, 180.65; MS *m/z* 358.1967 (29, calcd for $C_{22}H_{30}O_2S$ 358.1967), 317 (19), 301 (13), 247 (9), 161 (22), 123 (26), 84 (84), 57 (89), 41 (100). The structure was confirmed by 2D COSY and NOESY.

(3α,3aα,5*β*,7a*β*)-(±)-3-(2,2-Dimethylpropyl)-7a-methyl-5-[(phenylthio)methyl]hexahydro-2(3*H*)-benzofuranone (26a) was prepared from 1-methyl-1-vinyl-4-pentenyl acrylate according to the procedure outlined for the preparation of **10a** to afford **26a** in 50% yield as a white solid: m.p. 95−97 °C; ^{1}H NMR δ 0.924 (s, 9 H), 1.130 (dd, J = 1.5, 14.4 Hz, 1 H), 1.344 (s, 3 H), 1.400−1.736 (m, 5 H), 1.818−2.243 (m, 6 H), 3.246 (t, J = 11.1 Hz, 1 H), 7.252−7.387 (m, 5 H); ^{13}C NMR δ 18.76, 23.78, 29.42, 30.59, 31.91, 33.09, 41.08, 41.98, 42.65, 44.71, 50.52, 85.96, 127.24, 129.08, 132.01, 134.77, 178.63; MS *m/z* (relative intensity) 346.1975 (100, calcd for $C_{21}H_{30}O_2S$ 346.1967), 331 (10), 237 (28), 110 (95), 57 (97). The structure was confirmed by 2D NOESY.

(3α,3aα,5*β*,7a*β*)-(±)-3-(2,2-Dimethylpropyl)-7a-methyl-5-[1-methyl-1-(phenylthio)ethyl]hexahydro-2(3*H*)-benzofuranone (26b) was prepared from 1,5-dimethyl-1-vinyl-4-hexenyl acrylate according to the procedure outlined for the preparation of **10a** to afford **26b** in 40% yield as a colorless oil: ^{1}H NMR δ 0.948 (s, 9 H), 1.177 (dd, J = 3.0, 14.4 Hz, 1 H), 1.228 (s, 3 H), 1.248 (s, 3 H), 1.305 (s, 3 H), 1.330−1.425 (m, 1 H), 1.538−1.714 (m, 4 H), 1.879 (dd, J = 5.1, 14.4 Hz, 1 H), 2.039−2.128 (m, 3 H), 2.288 (ddd, J = 3.3, 5.1, 13.8 Hz, 1 H), 7.299−7.379 (m, 3 H), 7.470−7.521 (m, 2 H); ^{13}C NMR δ 18.32, 24.57, 25.25, 27.15, 27.50, 29.51, 30.52, 36.74, 39.84, 42.34, 47.14, 52.23, 53.50, 83.20, 128.64, 128.94, 131.80, 137.67, 179.89; MS *m/z* (relative intensity) 374.2275 (16, calcd for $C_{23}H_{34}O_2S$ 374.2280), 265 (100), 209 (27), 135 (58), 110 (47), 93 (28), 57 (33). The structure was confirmed by 2D COSY and NOESY.

(3α,3aα,4aα,5α,8aα,9a*β*)-(±)-3-(2,2-Dimethylpropyl)-9,9-dimethyl-5-(phenylthio)decahydronaphtho[2,3-b]furan-2(3*H*)-one (27) was prepared from 2-(2-cyclohexenyl)-2-methyl-1-vinylpropyl acrylate according to the procedure outlined for the preparation of **10a** to afford **27** in 30% yield as a colorless oil: ^{1}H NMR δ 0.890 (s, 9 H), 0.915 (s, 3 H), 1.066 (s, 3 H), 1.158 (dd, J = 3.2, 14.4 Hz, 1 H), 1.21−1.357 (m, 1 H), 1.557−1.638 (m, 3 H), 1.686−1.829 (m, 5 H), 1.877 (dd, J = 5.2, 14.4 Hz, 1 H), 1.959 (ddd, J = 3.6, 4.0, 13.2 Hz, 1 H), 2.074 (ddd, J = 3.2, 4.8, 12.4 Hz, 1 h), 2.143−2.176 (m, 1 H), 3.397 (br, 1 H), 3.771 (d, J = 11.2 Hz, 1 H), 7.198−7.301 (m, 3 H), 7.368−7.392 (m, 2 H); ^{13}C NMR δ 20.35, 21.63, 22.49, 25.32, 25.66, 29.45, 30.16, 30.46, 35.81, 37.61, 41.93, 42.60, 43.77, 45.98, 51.12, 86.40, 127.17, 129.10, 132.24, 135.55, 179.87; HRMS calcd for $C_{25}H_{36}O_2S$ 400.2436, found 400.2442. The structure was confirmed by 2D COSY, NOESY and HETCOR.

Acknowledgment. We are grateful for financial support provided by the National Science Foundation (CHE-9220639).

Supporting Information Available: Spectroscopic data for the three isolated isomers of **3b**, the two phenyl sulfides derived from **20** and **22**, and the diene and triene precursors to **3a**, **6**, **7a**−**c**, **9b**−**h**, **16**, **17**, **20**, **22**, **26a,b**, and **27** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9601898