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Cyclizations in the homolytic reactions of unsaturated nitriles with *tert*-butylmercury halides in the presence of proton donors†

Glen A. Russell* and Ping Chen

Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA

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ABSTRACT: Cyclizations are observed in the homolytic reactions of *t*-BuHgI with $CH_2{=}CHCH_2YCH_2CN$ [Y = CH_2, O, CMe_2, $C(CO_2Et)_2$, NCH_2CN] and $CH_2{=}CHCH_2CH_2YCH_2CN$ [Y = CH_2, O, $C(CO_2Et)_2$] in Me_2SO in the presence of hydriodic acid. Only with Y = $C(CO_2Et)_2$ does the adduct radical, *t*-$BuCH_2\dot{C}HCH_2YCH_2CN$, undergo facile 5-*exo* cyclization in the absence of a proton donor. The other 5-*exo* and all 6-*exo* cyclizations require substrate protonation to yield *t*-$BuCH_2\dot{C}H(CH_2)_nYCH_2C{\equiv}NH^+$ (n = 1, 2), which cyclizes readily to the iminium radical cation followed by electron transfer with I^- or *t*-$BuHgI_2^-$ to form the imine as a precursor to the cyclopentanone or cyclohexanone upon hydrolysis. For $CH_2{=}CHCH_2C(CO_2Et)_2CH_2CN$ the formation of the cyclopentanone is dramatically promoted by NH_4I in the dark in the absence of any other acid. In this case, where cyclization of the adduct radical occurs readily without substrate activation, protonation of the cyclized iminyl radical allows the electron transfer with I^- or *t*-$BuHgI_2^-$ to occur with regeneration of *t*-Bu$^\bullet$. A similar effect is observed with $CH_2{=}CHCH_2C(CO_2Et)_2CH_2N_3$ where only a slow reaction is observed upon photolysis with *t*-BuHgI in the absence of NH_4I, although apparently cyclization of *t*-$BuCH_2\dot{C}HCH_2C(CO_2Et)_2CH_2N_3$ (with loss of N_2) occurs readily. In the presence of NH_4I the cyclized aminyl radical can be protonated and the resulting amine radical cation readily reduced by I^- or *t*-$BuHgI_2^-$ to continue a chain process. With the thioesters $CH_2{=}CHCH_2YCH_2C(O)SPh$ [Y = O, CH_2, CMe_2, $C(CO_2Et)_2$], significant cyclization upon photolysis with *t*-BuHgX occurred only for Y = $C(CO_2Et)_2$. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: unsaturated nitriles; homolytic reactions; cyclization; *tert*-butylmercury halides; proton donors

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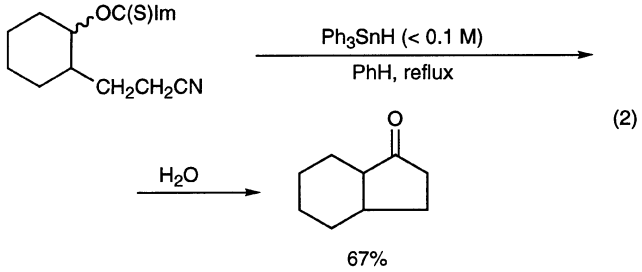
INTRODUCTION

tert-Butylmercury halides will form the 1:1 adducts with terminal alkenes when irradiated with a fluorescent sunlamp at 35 °C in Me_2SO solution:[1]

$$CH_2{=}CHBu + t\text{-}BuHgX \xrightarrow{h\nu,5\ h} t\text{-}BuCH_2CH(HgX)Bu \quad (1)$$
$$X = Cl\ (40\%), X = I\ (43\%)$$

The adduct can be reduced to the alkane by $NaBH_4$ or converted to *t*-$BuCH_2CH(SPh)Bu$ in 95% yield by photolysis with Ph_2S_2. As measured by $(t\text{-}Bu)_2NO^\bullet$ inhibition, the rate of adduct formation is only slightly greater (*ca* 40%) than the rate of formation of radicals trapped by the nitroxide. With 1,6-dienes or enynes the cyclized organomercurials are formed in free radical chain reactions with modest initial kinetic chain lengths (3–10) which increase for $CH_2{=}CHP(O)(OH)OCH_2CH{=}CH_2$, $CH_2{=}CHC(O)OC(Me_2)CH{=}CH_2$ or $CH_2{=}CHC(O)N(CH_2CH{=}CH_2)_2$ to 50–200, whereas dark reactions, initiated by *t*-BuHgI–KI at 25 °C,[2] give initial chain lengths of 4300 for the allyl vinylphosphonate and *ca* 20 000 for *N,N*-diallylacrylamide.[1] We have extended these studies to additive cyclizations of ω-unsaturated nitriles, azides and thioesters, functional groups recognized to participate in 5-*exo* cyclizations, primarily in the reactions of low concentrations of R_3SnH or molar equiv. of $Bu_3SnSnBu_3$ with appropriately substituted alkyl halides or thionocarbamates, e.g. according to the equation.[3–5]



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Radical cyclizations leading to cycloalkanones are also

†Electron Transfer Processes. Part 65.

**Deceased 1997, correspondence to:* M. Russell, Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA.
E-mail: grussell@iastate.edu

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$R'CH(Ph)NR^{\cdot} + H^+ \rightleftharpoons R'CH(Ph)NHR^{\cdot +}$

$R'CH_2\dot{C}HC{\equiv}N + H^+ \rightleftharpoons R'CH_2CH{=}C{=}NH^{\cdot +}$

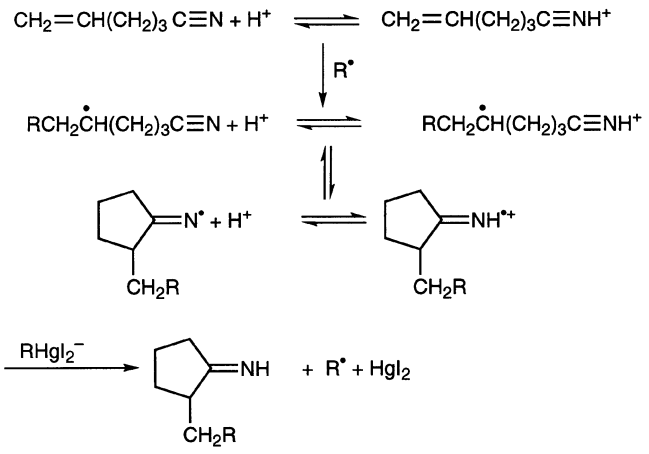
$R''NHR^{\cdot +} + R'HgI_2^- \rightarrow R''NHR + R'^{\cdot} + HgI_2$

$R'CH_2CH{=}C{=}NH^{\cdot +} + R'HgI_2^- \rightarrow R'CH_2CH{=}C{=}NH + R'^{\cdot} + HgI_2$

Scheme 1. R′ = *t*-Bu.

observed in the oxidative decarboxylation of ω-cyanocarboxylic acids,[6] in Mn(III) oxidations of β-diketones yielding, after an initial cyclization, 4- or 5-cyanoalkyl radicals,[7] and in the intramolecular addition of ketyls, or their trimethylsilyl derivatives, to γ- or δ-unsaturated nitriles.[8,9]

Initial experiments with *t*-BuHgX (X = Cl, I) and $CH_2{=}CH(CH_2)_3CN$ led only to the uncyclized 1:1 adducts in yields comparable to those observed for 1-hexene. This was not surprising because the 5-*exo* cyclization of $^{\cdot}CH_2(CH_2)_3CN$ is known to occur with a rate constant of only 4×10^3 s^{-1} at 25 °C, a value approximately 1/25th that of $^{\cdot}CH_2CH_2CH{=}CH_2$ and 1/60th that of $^{\cdot}CH_2(CH_2)_3CH{=}CH_2$.[10] The 5-*exo* cyclization of $^{\cdot}CH_2(CH_2)_3CN$ is only slightly exothermic,[11] and although the cyclization is irreversible at −14 °C,[10b] ring opening of the cyclopentyliminyl radical occurs readily at >250 °C.[11,12] Moreover, homolytic 1,4-shifts of cyano groups have been observed to occur readily at 25–80 °C for $^{\cdot}CH_2(CH_2)_2C(R^1)(R^2)CN$, particularly when R^1 = OH or alkyl and R^2 = alkyl, aryl or CO_2Et.[13,14] In view of these results, we reasoned that if reversible cyclization was occurring, the cyclized radical should be converted to the imine by the presence of a proton donor and iodide ion, a combination that has proven to be efficient for the reductive alkylation of imines[15] or α,β-unsaturated nitriles,[16] even with NH_4^+ as the proton donor (Scheme 1). Indeed, NH_4I was an excellent promoter for additive cyclizations of $CH_2{=}CHCH_2C(CO_2Et)_2CH_2CN$ or $CH_2{=}CH(CH_2)_3N_3$ in Me_2SO but with $CH_2{=}CH(CH_2)_3CN$ a much stronger acid (hydriodic acid) was required to bring about cyclization. Apparently, for $^{\cdot}CH_2(CH_2)_3CN$ cyclization is too slow for protonation of the cyclized radical to promote a homolytic chain reaction significantly and promotion is observed only with acids strong enough to give both substrate and radical activation (Scheme 2).[17]

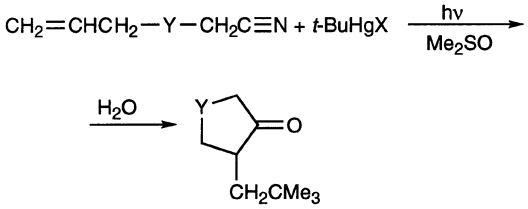


Scheme 2. R = *t*-Bu.

RESULTS AND DISCUSSION

γ-Cyanoalkenes

Table 1 summarizes results for the reaction



(3)

1, **a**, Y = CH_2
b, Y = O
c, Y = $C(Me)_2$
d, Y = NCH_2CN
e, Y = $C(CO_2Et)_2$

In the presence of KI, NH_4I or PTSA, small amounts of **1a** were observed in addition to the uncyclized 1:1 adduct. However, significant amounts of **1a** were formed only in the presence of 2–4 equiv. of hydriodic acid or PTSA and iodide salts. It does not appear that non-ionized HI is acting as a chain transfer agent because *t*-$Bu(CH_2)_4CN$ is not observed as a reaction product. Apparently substrate protonation (Scheme 2) leads to promotion of the cyclization reaction leading to the easily reduced iminium ion.

Similar results were observed for $CH_2{=}CHCH_2OCH_2CN$, $CH_2{=}CHCH_2C(Me)_2CH_2CN$ and $CH_2{=}CHCH_2N(CH_2CN)_2$ with significant yields of **1b–d** observed only in the presence of hydriodic acid (Table 1). However, with $CH_2{=}CHCH_2C(CO_2Et)_2CH_2CN$ the formation of **1e** was significant with *t*-BuHgI alone, with the yield improved only slightly by the presence of hydriodic acid. With the *gem*-diester, cyclization must occur readily to yield the iminyl radical which is trapped by *t*-BuHgI to form the imine and/or its Hg(II) salt as a precursor to **1e**. The reaction will now occur in the dark in the presence of I^- [The thermal formation of *t*-$Bu^{\cdot}$ at 25 °C from *t*-BuHgI–I^- may involve comproportionation to form the labile $(t\text{-Bu})_2Hg^2$], and under this condition there is a dramatic promotion by the presence of NH_4^+. The iminyl radical is apparently protonated by NH_4^+ to form the iminium ion, which reacts with *t*-$BuHgI_2^-$ or I^- (Scheme 1) more readily than the iminyl radical reacts with *t*-BuHgI. The dark reactions with NH_4I are inhibited for 2–3 weeks by the

Table 1. Photolysis of *t*-BuHgX with $CH_2{=}CHCH_2{-}Y{-}CH_2CN$[a]

Y	X (equiv.)	Additive (equiv.)	Time (h)	Product (%)[b]
CH_2	Cl (4)	KI (8)	16	**1a** (4)
CH_2	Cl (4)	NH_4I (8)	12	**1a** (8)
CH_2	Cl (4)	PTSA (4)	12	**1a** (8)
CH_2	I (4)	PTSA (4)	12	**1a** (7)
CH_2	I (4)	PTSA (4), KI (4)	12	**1a** (20)
CH_2	I (4)	Aq. HI (4)	12	**1a** (41)
CH_2	I (4)	Aq. HI (2)	20	**1a** (55)
O	I (4)	Aq. HI (2)	24	**1b** (60)
$C(Me)_2$	I (4)	NH_4I (4)	12	**1c** (10)
$C(Me)_2$	I (4)	Aq. HI (2)	12	**1c** (55)
NCH_2CN	I (4)	Aq. HI (4)	12	**1d** (34)
$C(CO_2Et)_2$	I (4)	None	12	**1e** (74)
$C(CO_2Et)_2$	I (4)	Aq. HI (2)	8	**1e** (80)
$C(CO_2Et)_2$	I (4)	KI (2)	24	**1e** (10)[c]
$C(CO_2Et)_2$	I (4)	NH_4I (2)	18	**1e** (78)[c]

[a] 0.13 M nitrile in Me_2SO-d_6 irradiated by a 275 W fluorescent sunlamp at 35–40 °C. The use of Me_2SO-d_6 allowed the reactions to be monitored by ^1H NMR.
[b] By ^1H NMR with $PhCH_3$ as an internal standard after workup with aq. $Na_2S_2O_3$.
[c] Dark reactions at 25 °C.

presence of 10 mol% of $(t\text{-Bu})_2NO^{\bullet}$, indicating an appreciable kinetic chain length for the homolytic reaction. 4,4-Dimethyl-5-hexenenitrile was much less reactive than its 3,3-dimethyl isomer, presumably because of steric hindrance in the addition of *t*-Bu$^{\bullet}$ to form a neopentyl-type radical. Even in the presence of hydriodic acid only a 10% yield of 3,3-dimethyl-2-(2,2-dimethylpropyl)cyclopentanone was observed under the conditions employed in Table 1. 2,2-Dimethyl-5-hexenenitrile also gave a lower yield of the cyclopentanone (34%) than the 3,3-dimethyl isomer.

δ-Cyanoalkenes

6-*Exo* cyclizations of $^{\bullet}CH_2(CH_2)_4CN$ routinely occur less efficiently than 5-*exo* cyclizations of the 4-cyano homologs, in part because of 1,5-hydrogen atom shifts:[5,18,19]

$$t\text{-BuCH}_2\dot{C}H(CH_2)_4CN \longrightarrow t\text{-Bu}(CH_2)_4\dot{C}HCN \quad (4)$$

In the presence of NH_4I, 1-cyanoalkyl radicals are reduced by both the reactions of Scheme 1 and by the reactions[15]

$$R\dot{C}HCN + t\text{-BuHgI}_2^- \longrightarrow RCH(CN)HgI_2^- + t\text{-Bu}^{\bullet} \quad (5)$$

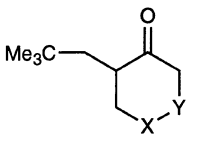
$$RCH(CN)HgI_2^- + NH_4^+ \longrightarrow RCH_2CN + NH_3 + HgI_2 \quad (6)$$

Table 2. Photolysis of *t*-BuHgI with $CH_2{=}CHCH_2{-}X{-}Y{-}CH_2CN$[a]

X	Y	Products (%)[b]	
CH_2	CH_2	**2a** (9)	**3a** (29)
CH_2	O	**2b** (25)	**3b** (12)
CH_2	$C(CO_2Et)_2$	**2c** (34)	**3c** (26)
$C(CO_2Et)_2$	CH_2	**2d** (22)	**3d** (33)

[a] See Table 1. Reactions were photolyzed for 16 h.
[b] After hydrolysis with aq. $Na_2S_2O_3$; see Table 1.

Reactions of δ-cyanoalkenes ($CH_2{=}CHCH_2{-}X{-}Y{-}CH_2C{\equiv}N$) with 4 equiv. of *t*-BuHgI and 2 equiv. of hydriodic acid in Me_2SO with sunlamp irradiation for 16 h thus formed a mixture of the cyclohexanones **2** and the uncyclized reductive *tert*-butylation products **3** (Table 2):



2

$Me_3CCH_2CH_2CH_2\text{-}X\text{-}Y\text{-}CH_2C{\equiv}N$

3

a, X = Y = CH_2
b, X = CH_2, Y = O
c, X = CH_2, Y = $C(CO_2Et)_2$
d, X = $C(CO_2Et)_2$; Y = CH_2

Only in the formation of **2b**/**3b** and **2c**/**3c** did the cyclized product predominate over the 1,5-hydrogen atom transfer product. The formation of **3** must be a result of the 1,5-hydrogen atom rearrangement because analogous reductive alkylation products were not observed with γ-cyanoalkenes or 1-hexene. In addition, photolysis of $CH_2{=}CH(CH_2)_3CMe_2CN$ with *t*-BuHgI–HI produced mainly the uncyclized 1:1 adduct (42%), *ca* 2% of the

cycloalkanone and no significant amounts of the reductive alkylation product analogous to **3**.

Two ε-cyanoalkenes were examined neither of which gave any indication of 7-*exo* cyclization. Photolysis of $CH_2{=}CHCH_2CH_2C(CO_2Et)_2CH_2CH_2CN$ with *t*-BuHgI–HI gave the 1:1 adduct in 45% yield together with 19% of the reductive alkylation product, *t*-$Bu(CH_2)_3C(CO_2Et)_2CH_2CH_2CN$, possibly from a 1,5- or 1,6-hydrogen atom transfer. With $CH_2{=}CHCH_2OCH_2C(Me)_2CH_2CN$ photolysis with *t*-BuHgI–HI for 7 h gave *ca* 90% of *t*-$BuCH_2CH{=}CH_2$ from a β-elimination process. β-Elimination in the reactions of *t*-BuHgX with allyl alcohol and its derivatives has been previously observed to proceed via *t*-$BuCH_2CH(HgX)CH_2OY$ with Y = H, Ph, Ac, Bz.[20,21] Similar reactions occur for propargyl alcohol derivatives. The elimination appears to be an E_2 process which is promoted by nucleophiles such as I^-.[20]

Other 5-*exo*-cyclization

Cyclizations involving thio esters were examined because the formation of $(R^1)(R^2)C(O^{\cdot})SPh$ and β-elimination of $PhS^{\bullet}$ should be irreversible. Intermolecular radical substitution in HC(O)SPh has been reported to occur in low yield upon photolysis with $PhO(CH_2)_4I$ in the presence of $Bu_3SnSnBu_3$,[22] while analogous intramolecular cyclizations involving δ- or ε-halo *S*-phenyl thioesters gave good yields of cyclized products, particularly with *gem*-disubstituted ω-iodo thioesters.[23]

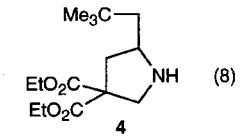
The allyl ethers $CH_2{=}CHCH_2OCH_2C(O)X$ with X = PhS, OH or OEt were examined because $CH_2{=}CHCH_2OCH_2CN$ had given a good cyclization reaction (Table 1). However, photolysis with *t*-BuHgCl initially formed only the 1:1 uncyclized adducts. In PhH the adducts were stable to further photolysis and could be isolated or reduced by $NaBH_4$ to give the reductive alkylation products. In Me_2SO the adducts decomposed to form *t*-$BuCH_2CH{=}CH_2$ without any indication of the formation of cyclized products. Since cyclization by the combination of the reactions in Scheme 3 still seemed reasonable in the absence of a β-elimination processes, we examined the *S*-phenyl 5-hexenethioates $CH_2{=}CHCH_2YCH_2C(O)SPh$ with Y = CH_2, CMe_2 and $C(CO_2Et)_2$. Although only a trace of **1a** was observed with Y = CH_2, a modest 18% yield of **1c** was observed with Y = CMe_2 while a fairly good yield (65%) of **1e** was obtained with Y = $C(CO_2Et)_2$ by photolysis with 4 equiv. of *t*-BuHgCl in Me_2SO at 35–40 °C for 18 h. We conclude that the rates of 5-*exo* cyclization are greater for the nitriles than for the *S*-phenyl thioates and that in both systems the rates of cyclization of *t*-$BuCH_2\dot{C}HCH_2YCH_2Q$ [Q = CN,C(O)SPh] increase from Y = CH_2 to CMe_2 to $C(CO_2Et)_2$, paralleling the substituent effects noted with Q = $CH{=}CH_2$.[1] The effect of *gem*-diester substitution at C-3 in 5-hexenyl radical cyclizations is significant and apparently more important than *gem*-dimethyl substitution; the latter has been previously recognized to enhance cyclizations in 3-butenyl,[24] 4-pentenyl,[25] 5-hexenyl[26] or *t*-$BuCH_2\dot{C}HC(O)OC(Me)_2CH{=}CH_2$ radicals.[1] A similar effect apparently occurs in 6-*exo* cyclizations as judged from the results with δ-cyanoalkenes. In the 5-hexenyl cases the effect of substitution at C-3 is presumably a result of rotamer populations with the sickle conformation required for a radical cyclization more highly populated with ester substituents.[25b,27]

Cyclization was also observed upon photolysis of *t*-BuHgCl with $CH_2{=}CHCH_2C(CO_2Et)_2CH_2N_3$ in Me_2SO in the presence of NH_4I. Azides are known to be attacked by radicals to yield aminyl radicals, particularly by $Bu_3Sn^{\cdot}$:[28]

$$RN_3 + Bu_3Sn^{\bullet} \longrightarrow R\dot{N}SnBu_3 + N_2 \qquad (7)$$

In the case of attack of *t*-$Bu^{\cdot}$ upon $CH_2{=}CHCH_2C(CO_2Et)_2CH_2N_3$, it was not clear if the initial point of attack would be at the azide group or at the carbon–carbon double bond.[29] The product observed (**4**) in 50% yield clearly requires initial attack at the carbon–carbon double bond followed by cyclization with the loss of nitrogen:

t-BuHgCl (2 equiv) + $CH_2{=}CHCH_2C(CO_2Et)_2CH_2N_2$ —(NH_4I (2 equiv), Me_2SO, 5 h, hv)→



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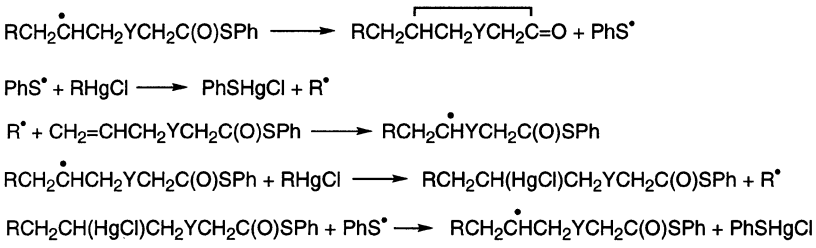
Little reaction was observed in the absence of NH_4I while the azide was destroyed by the use of PTSA or



Scheme 3. R = *t*-Bu.

hydriodic acid as promoters. The reaction appears to fit Scheme 1 where the aminyl radical formed by addition followed by cyclization reacts slowly with *t*-BuHgX to propagate the chain reaction. In the presence of NH_4^+ the aminyl radical can be protonated to give an aminium radical cation readily reduced to the amine by iodide ion or *t*-$BuHgI_2^-$. Either reaction continues the chain because iodine atom readily displaces *t*-Bu$^\bullet$ from *t*-BuHgI.

Although cyclizations in the photolysis of *t*-BuHgCl with $CH_2{=}CHC(O)OCMe_2CH{=}CH_2$, $CH_2{=}CHC(O)OCMe_2C{\equiv}CH$ or $CH_2{=}CHC(O)N(CH_2CH{=}CH_2)_2$ occur, the corresponding cyclizations in the reactions of $CH_2{=}CHC(O)OCMe_2CN$ or $CH_2{=}CHC(O)N(CH_2CN)_2$ were not observed. Reactions with *t*-BuHgI–KI in the dark formed the uncyclized 1:1 adducts in high yield whereas reactions in the presence of NH_4I, PTSA or hydriodic acid formed only their protonolysis products, *t*-$BuCH_2CH_2C(O)OCMe_2CN$ or *t*-$BuCH_2CH_2C(O)N(CH_2CN)_2$, in essentially quantitative yields.[1] In a similar fashion, $CH_2{=}CHC(O)OCH_2C(O)SPh$ formed only the uncyclized 1:1 adduct which could be protonated or reduced by Et_3SiH to *t*-$BuCH_2CH_2C(O)CH_2C(O)SPh$. Even photolysis of the adduct with Ph_2S_2, a process which led to cyclization for *t*-$BuCH_2CH(HgI)C(O)OCH_2CH{=}CH_2$ or *t*-$BuCH_2CH(HgI)C(O)OCH_2C{\equiv}CH$, failed to yield cyclized products. 5-*Exo* cyclizations of ester or amide radicals are more difficult than the cyclizations of simple 5-hexenyl radicals while the —C≡N or —C(O)SPh groups are less reactive in 5-*exo* attack than —CH═CH_2 or —C≡CH groups.

Reaction of *t*-BuHgI–I^- with $CH_2{=}CHC(O)OCH_2CH_2N_3$ in Me_2SO failed to occur in the dark at room temperature. This was surprising because various acrylate esters, including $CH_2{=}CHCO_2CH_2CH_2Br$, gave essentially quantitative yields of the 1:1 adduct in 0.5–1 h by a free radical chain reaction.[1] Photolysis of $CH_2{=}CHCO_2CH_2CH_2N_3$ with *t*-BuHgI–I^- yielded only the reductive alkylation product, although in low yield (24% after 6 h), even in the absence of a proton donor. This suggests that 1,5-hydrogen atom transfer is greatly facilitated by the azido group to yield *t*-$BuCH_2CH_2CO_2CH_2CHN_3^\bullet$, which does not readily continue a chain reaction with *t*-BuHgI–I^- but which under forcing conditions can be converted to *t*-$BuCH_2CH_2CO_2CH_2CH_2N_3$.

EXPERIMENTAL

Substrates (0.5–1 mmol), *t*-BuHgX and any other reagents were added to Pyrex tubes containing 4–10 ml of deoxygenated Me_2SO under a nitrogen atmosphere. The solutions were stirred in the dark at *ca* 25 °C with the tube wrapped in aluminum foil or irradiated with a 275 W Sylvania fluorescent sunlamp *ca* 25 cm from the reaction tube at 35–40 °C. Reactions were conveniently monitored by ^{1}H NMR by the use of Me_2SO-d_6 as solvent. Upon completion of the reaction the products were poured into a saturated aqueous $Na_2S_2O_3$ solution and extracted by CH_2Cl_2. The products were analyzed by GC–MS and ^{1}H NMR using toluene as an internal standard for yield determination. Products were isolated by flash column or thin-layer chromatography using silica gel with hexane–ethyl acetate as the eluent.

^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz and are reported in ppm from internal Me_4Si or the central line of $CDCl_3$ at 77.00 ppm, respectively. Electron ionization (EI) mass spectra at 70 eV were obtained in the GC mode with a Finnegan 4000 spectrometer and in the HR mode with a Kratos MS-50 spectrometer. FTIR spectra were recorded on IBM 1898 or Digital FTS-7 spectrometers.

The preparation of *t*-BuHgX has been described previously.[1,2] Substrates employed were synthesized by standard methods and are described in the Supplementary Material.

2-(2,2-Dimethylpropyl)cyclopentanone (1a). The product was isolated as a liquid: IR (neat), 2958, 2868, 1742 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 0.92 (s, 9 H), 1.05 (dd, J = 14.1, 9.0 Hz, 1 H), 1.43–1.57 (m, 1 H), 1.68–1.82 (m, 1 H), 1.88 (dd, J = 14.1, 2.4 H, 1 H), 1.92–2.12 (m, 3 H), 2.25–2.43 (m, 2 H); ^{13}C NMR ($CDCl_3$), δ 20.80, 29.77, 30.47, 32.74, 37.37, 44.13, 46.77, 221.85; MS, *m/z* 154.1361 (calculated for M^+ 154.1358), 139 (14), 125 (11), 112 (28), 97 (29), 83 (32), 57 (100).

4-(2,2-Dimethylpropyl)tetrahydrofuran-3-one (1b). The product was isolated as a liquid: ^{1}H NMR ($CDCl_3$), δ 0.91 (s, 9 H), 1.16 (dd, J = 14.4, 9.6 Hz, 1 H), 1.87 (dd, J = 14.4, 2.4 Hz, 1 H), 2.39–2.50 (m, 1 H), 3.69 (dd or t, J = 9.6 Hz, 1 H), 3.74 (dd, J = 17.1, 0.6 Hz, 1 H), 4.08 (dd, J = 17.1, 1.2 Hz, 1 H), 4.60 (dd or t, J = 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$), δ 29.52, 30.24, 41.91, 44.98, 70.33, 74.28, 217.11; MS, *m/z* 156.1148 (4) (calculated for M^+ 156.1150), 141 (3), 114 (5), 83 (23), 57 (100).

2-(2,2-Dimethylpropyl)-4,4-dimethylcyclopentanone (1c). The compound was isolated as a liquid: ^{1}H NMR ($CDCl_3$), δ 0.91 (s, 9 H), 1.07 (dd, J = 13.8, 9.6 Hz, 1 H), 1.07 (s, 3 H), 1.17 (s, 3 H), 1.41–1.49 (m, 1 H), 1.89 (dd, J = 13.8, 2.4 Hz, 1 H), 1.95–2.33 (m, 4 H); ^{13}C NMR ($CDCl_3$), δ 27.92, 29.74, 29.78, 30.53, 34.10, 45.31, 45.65, 47.23, 52.49, 221.96; MS, *m/z* 182.1675 (16) (calculated for M^+ 182.1671), 167 (13), 125 (85), 111 (22), 98 (17), 83 (26), 69 (29), 57 (100).

5-(2,2-Dimethylpropyl)-2,2-dimethylcyclopentanone. The product was isolated as a liquid: ^{1}H NMR ($CDCl_3$), δ 0.92 (s, 9 H), 0.94 (s, 3 H), 1.08 (dd, J = 13.8, 9.3 Hz, 1 H), 1.08 (s, 3 H), 1.46–1.70 (m, 2 H), 1.78–1.85 (m, 1 H), 1.89 (dd, J = 14.1, 2.4 Hz, 1 H), 2.02–2.12 (m, 1 H), 2.20–2.30 (m, 1 H); ^{13}C NMR ($CDCl_3$), δ 23.76, 24.70, 28.98, 29.84, 30.64, 36.84, 44.36, 45.55, 46.11, 225.12;

MS, *m/z* 182.1669 (26) (calculated for M^+ 182.1671), 167 (16), 125 (58), 112 (22), 111 (19), 83 (22), 57 (100).

2-(2,2-Dimethylpropyl)-3,3-dimethylcyclopentanone. The ketone was a solid, m.p. 42–44 °C: ^{1}H NMR ($CDCl_3$), δ 0.71 (s, 3 H), 0.88 (s, 9 H), 0.98 (dd, J = 13.8, 1.5 Hz, 1 H), 1.12 (s, 3 H), 1.52 (dd, J = 13.8, 6.9 Hz, 1 H), 1.72–1.82 (m, 3 H), 2.14 (ddd, J = 19.2, 10.8, 8.7 Hz, 1 H), 2.32 (dddd, J = 19.2, 8.4, 3.3, 1.2 Hz, 1 H); ^{13}C NMR, δ 21.22, 27.99, 29.45, 30.24, 34.75, 35.54, 36.33, 39.55, 57.04, 219.63; MS, *m/z* 182.1670 (7) (calculated for M^+ 182.1671), 167 (59), 153 (16), 125 (66), 111 (53), 70 (40), 57 (100).

1-(Cyanomethyl)-4-(2,2-dimethylpropyl)-3-pyrrolidinone (1d). The product was isolated as a liquid: ^{1}H NMR ($CDCl_3$), δ 0.92 (s, 9 H), 1.22 (dd, J = 14.4, 9.6 Hz, 1 H), 1.87 (dd, J = 14.1, 2.4 Hz, 1 H), 2.42–2.52 (m, 1 H), 2.59 (dd, J = 9.6, 8.8 Hz, 1 H), 2.91 (d, J = 16.5 Hz, 1 H), 3.36 (d, J = 16.5 Hz, 1 H), 3.49 (t, J = 8.1 Hz, 1 H), 3.76 (s, 2 H); ^{13}C NMR ($CDCl_3$), δ 29.54, 30.36, 42.12, 42.37, 46.61, 58.17, 58.21, 113.94, 213.91; MS, *m/z* 194.1417 (13) (calculated for M^+ 194.1419), 179 (28), 166 (15), 151 (13), 109 (28), 69 (64), 57 (100).

2-(2,2-Dimethylpropyl)-4,4-bis(ethoxycarbonyl)cyclopentanone (1e). The product was isolated as a liquid: ^{1}H NMR ($CDCl_3$), δ 0.92 (s, 9 H), 1.08 (dd, J = 14.1, 9.3 Hz, 1 H), 1.28 (t, J = 7.2 Hz, 6 H), 1.92 (dd, J = 14.1, 2.4 Hz, 1 H), 1.96 (t, J = 12.6 Hz, 1 H), 2.24–2.35 (m, 1 H), 2.73 (d, J = 19.2 Hz, 1 H), 2.92–3.05 (m, 2 H), 4.19–4.30 (m, 4 H); ^{13}C NMR ($CDCl_3$), δ 13.94, 29.67, 30.36, 39.08, 44.16, 44.25, 45.32, 55.06, 61.97, 170.75, 171.03, 215.94; MS, *m/z* 298.1787 (15) (calculated for M^+ 298.1780), 283 (14), 253 (11), 241 (18), 200 (100), 154 (93), 69 (92), 57 (55).

8,8-Dimethylnonanenitrile (3a). The product was isolated as a liquid: ^{1}H NMR ($CDCl_3$), δ 0.86 (s, 9 H), 1.12–1.76 (m, 10 H), 2.34 (t, J = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$), δ 17.12, 24.22, 25.37, 28.70, 29.36, 29.66, 30.25, 44.04, 119.86.

4-(2,2-Dimethylpropyl)-dihydro-2H-pyran-3-(4H)-one (2b). The product was isolated as a liquid: IR (neat), 2959, 2869, 1724, 1476, 1367, 483 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 0.90 (s, 9 H), 0.94 (dd, J = 14.1, 4.8 Hz, 1 H), 1.76–1.89 (m, 1 H), 2.17–2.28 (m, 2 H), 2.44–2.57 (m, 1 H), 3.81–3.98 (m, 2 H), 4.02 (J_{AB} = 20.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$), δ 29.45, 30.65, 34.34, 41.46, 43.82, 66.07, 74.60, 209.35; MS, *m/z* 169.1224 (calculated for M^+ 169.1228), 169 (8), 155 (10), 113 (25), 73 (20), 69 (15), 57 (100).

2-(2,2-Dimethylpropyl)-5,5-bis(ethyoxycarbonyl)cyclohexanone (2c). The material was isolated as a liquid: ^{1}H NMR ($CDCl_3$), δ 0.86 (s, 9 H), 1.15–1.32 (m, 7 H), 1.48–1.61 (m, 1 H), 2.02–2.28 (m, 4 H), 2.36–2.44 (m, 1 H), 2.62 (dd, J = 14.1, 0.9 Hz, 1 H), 2.97 (dd, J = 14.1, 2.1 Hz, 1 H), 4.11–4.29 (m, 4 H); ^{13}C NMR ($CDCl_3$), δ 13.87, 29.32, 29.92, 30.53, 31.30, 41.68, 45.04, 46.11, 57.70, 61.67, 61.71, 170.18, 170.30, 207.52; MS, *m/z* 312.1928 (10) (calculated for M^+ 312.1937), 297 (27), 255 (54), 239 (27), 211 (24), 181 (44), 175 (58), 138 (43), 57 (100).

3,3-Bis(ethoxycarbonyl)-8,8-dimethylnonanenitrile (3c). The material was isolated as a liquid: ^{1}H NMR ($CDCl_3$), δ 0.87 (s, 9 H), 1.15–1.35 (m, 12 H), 2.06–2.12 (m, 2 H), 2.95 (s, 2 H), 4.25 (q, J = 7.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$), δ 13.88, 21.72, 24.51, 24.87, 29.24, 30.16, 32.69, 43.66, 55.30, 62.23, 116.31, 168.82; MS, *m/z* 311.2087 (7) (calculated for M^+ 311.2096), 296 (86), 254 (20), 238 (32), 199 (84), 182 (88), 154 (45), 97 (30), 57 (100).

2-(2,2-Dimethylpropyl)-4,4-bis(ethoxycarbonyl)cyclohexanone (2d). The compound was isolated as a liquid: ^{1}H NMR ($CDCl_3$), δ 0.76 (dd, J = 14.4, 4.5 Hz, 1 H), 0.98 (s, 9 H), 1.26 (t, J = 7.2 Hz, 3 H), 1.32 (t, J = 7.2 Hz, 3 H), 1.87 (t, J = 13.2 Hz, 1 H), 2.11 (dt, J = 13.2, 5.1 Hz, 1 H), 2.25 (dd, J = 14.1, 4.8 Hz, 1 H), 2.37–2.75 (m, 5 H), 4.19 (q, J = 7.2 Hz, 2 H), 4.32 (dq, J = 7.2, 2.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$), δ 13.92, 14.07, 29.27, 30.53, 31.94, 38.21, 40.33, 40.67, 43.07, 54.75, 61.72, 170.47, 170.81, 210.06; MS, *m/z* 312.1941 (18) (calculated for M^+ 312.1936), 297 (26), 296 (28), 255 (61), 181 (49), 173 (100), 140 (20), 108 (23), 69 (80), 57 (83).

4,4-Bis(ethoxycarbonyl)-8,8-dimethylnonanenitrile (3d). The product was isolated as a liquid: ^{1}H NMR ($CDCl_3$), δ 0.86 (s, 9 H), 1.15–1.26 (m, 4 H), 1.27 (t, J = 7.2 Hz, 6 H), 1.82–1.87 (m, 2 H), 2.22–2.27 (m, 2 H), 2.38–2.43 (m, 2 H), 4.14–4.28 (m, 4 H); ^{13}C NMR ($CDCl_3$), δ 13.03, 14.02, 19.13, 28.87, 29.25, 30.31, 34.14, 44.23, 56.72, 61.60, 119.12, MS, *m/z* 311.2094 (2) (calculated for M^+ 311.2097), 296 (35), 266 (16), 254 (19), 181 (17), 173 (100), 108 (25), 57 (61).

2-(2,2-Dimethylpropyl)-4,4-bis(ethoxycarbonyl)pyrrolidine (4). The compound was isolated as a liquid: ^{1}H NMR, δ 0.95 (s, 9 H), 1.26 (t, J = 7.2 Hz, 6 H), 1.41 (dd, J = 14.1, 6.6 Hz, 1 H), 1.57 (dd, J = 13.8, 5.4 Hz, 1 H), 1.77 (dd, J = 13.5, 9.3 Hz, 1 H), 2.08 (br s, 1 H), 2.67 (dd, J = 13.2, 6.6 Hz, 1 H), 3.13 (d, J = 12.3 Hz, 1 H), 3.11–3.21 (m, 1 H), 3.63 (d, J = 12.6 Hz, 1 H), 4.16–4.26 (m, 4 H); ^{13}C NMR ($CDCl_3$), δ 13.97, 13.99, 30.03 ($\times$2), 43.33, 49.29, 54.70, 57.73, 61.49 ($\times$2), 61.57, 171.25, 172.25; MS, *m/z* 285.1940 (1) (calculated for M^+ 285.1940), 270 (2), 240 (9), 214 (100), 194 (7), 140 (14), 68 (10).

SUPPLEMENTARY MATERIAL

Synthesis and spectral properties of precursors employed (7 pages) can be found on the epoc website at http://www.wiley.com/epoc

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