1993

Reductive radical alkylations of substituted olefins by alkylmercury halides

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Iowa State University, 1993

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Reductive radical alkylations of substituted olefins by alkylmercury halides

by

Bing Zhi Shi

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa
1993

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INTRODUCTION

Free radical chemistry has a comparatively long history. Before the acceptance of the quadrivalence of carbon, various attempts were made to prepare trivalent carbon species like methyl and ethyl. Initial investigations involving reaction between alkyl iodide and zinc were thought to be successful,[1] but were subsequently branded as failure.[2] In fact free methyl and ethyl were transient radicals involved in the reactions, but because of their short lifetimes the radicals were not detected, and only the hydrocarbons formed by dimerization of the radicals were isolated. At the beginning of our century Gomberg discovered the stable triarylmethyl radicals,[3] and then in the 1920's Paneth[4] showed that the free alkyl radicals could have a short lifetime in the gas phase. Free radicals as intermediates in reactions in solution were largely unrecognized until 1937 when Hey and Waters[5] interpreted a number of reactions, which did not fit into the then developing electronic theory of organic chemistry, by suggesting that they involved the intermediacy of free radicals. The other contemporary pioneer Kharasch[6] also proposed free radicals as intermediates in certain reactions in solution, many involving organometallic species, but also in the addition of hydrogen bromide to alkenes. A detailed knowledge of alkene polymerization by a free radical pathway developed rapidly.

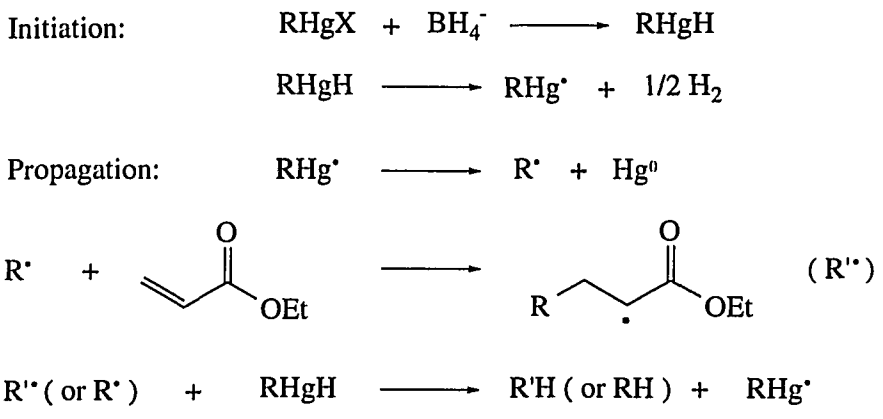
Within the last 20 years, ever increasing numbers of synthetic organic chemists have come to appreciate and understand the true values of working with "free, but well domesticated" preparative radical reactions.[7] At the level of selective functional group manipulation, the relative indifference of a free radical intermediate to its immediate molecular environment and to solvent has allowed application of a given transformation over a wide range of natural product families of vastly differing structural type and polarity. Even more importantly, at the fundamental level of strategy and design in organic

synthesis, key carbon-carbon bond forming reactions are now routinely considered in terms of a homolytic retrosynthetic disconnection.[8]

Organomercury compounds have been known since the middle of the past century, and they were one of the first types of organometallic compounds studied. However, due to the low reactivity of the mercury-carbon bond, their application in synthetic organic process was not important, and their utility was centered on the synthesis of other reactive organometallics. This low importance was even more diminished when the Grignard reagents were discovered at beginning of this century. However, in the past 20 years, organomercury compounds have again acquired interest in organic synthesis, in spite of their toxicity, in relation mainly to the solvomercuration reaction, which permits the preparation of functionalized organomercurials with high selectivity.[9]

One of the most widely studied free radical chain reactions of an organomercurial has been the alkaline sodium borohydride reduction of alkylmercury halides or carboxylates to yield the alkane or products derived from alkyl radical attack upon a suitable coreactant (Scheme I).[10]

Scheme I. The Giese Mercuric Hydride Process



The alkylmercury hydride generated by the reaction of an alkylmercury halide with borohydride readily decomposes to metallic mercury and the alkyl radical which gives an adduct radical upon attacking a coreactant, ethyl acrylate for instance (Scheme I). Either the adduct radical or the original alkyl radical abstracts hydrogen from alkylmercury hydride to give products with the adduct radical giving an intermolecular alkylation product and the alkyl radical giving the direct reduction product. An excess of alkene is usually required for intermolecular alkylation.

During the past several years, Russell has developed a series of free radical reactions in which alkylmercury halides or dialkylmercurials participate in the propagation step of a chain process.[11-33] Radical anion or neutral radicals which are easily oxidized ($D^{\bullet}$ or $D^{\bullet -}$, "donor radicals") will undergo a dissociative electron transfer reaction with alkylmercury halides. Alkylmercury halides also react readily with acceptor radicals ($A^{\bullet}$). Chain reactions ensue when the alkyl radical thus formed can regenerate a donor or an acceptor radical (reaction 1 and 2).

$$RHgX + D^{\bullet}\ (D^{\bullet -}) \longrightarrow R^{\bullet} + Hg^{0} + X^{-} + D^{+}\ (D) \qquad (1)$$

$$RHgX + A^{\bullet} \longrightarrow R^{\bullet} + AHgX \qquad (2)$$

Substitution involving S_H2 process:

Scheme II. S_H2 Process

$$R^{\bullet} + Y{-}Q \longrightarrow RY + Q^{\bullet} \quad (\text{either } D^{\bullet} \text{ or } A^{\bullet})$$

$$D^{\bullet} + RHgX \longrightarrow R^{\bullet} + Hg^{0} + X^{-} + D^{+}$$

$$A^{\bullet} + RHgX \longrightarrow R^{\bullet} + AHgX$$

The S_H2 reactions of alkyl radicals generated from alkylmercurials involve the formation of donor or acceptor radicals (Scheme II).[24,30,38]

Substitution by addition-elimination:

The radical addition-elimination sequence with alkylmercury halides occurs with a variety of leaving groups such as HgX, Bu_3Sn, PhS, $PhSO_2$, and halogens (reaction 3).[13,15,16]

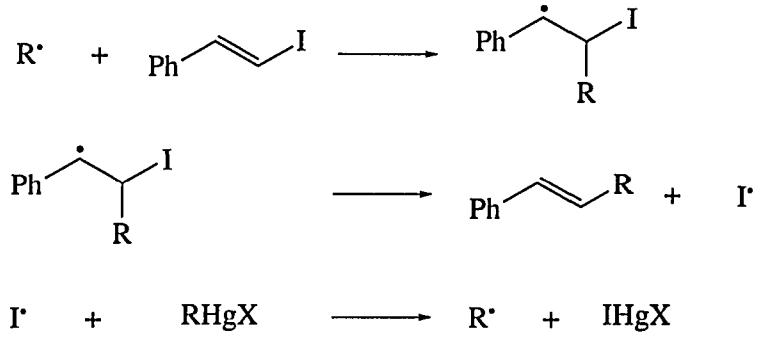
$$R'CH{=}CHQ + RHgX \longrightarrow R'CH{=}CHR + QHgX \ (\text{or } QX + Hg^0) \qquad (3)$$

The addition-elimination mechanism is illustrated by the reaction of (E)-β-iodostyrene with alkylmercury halide (Scheme III). Similar reactions are recognized for substituted alkynes and for allyl or propargyl derivatives.[23,29,31]

Addition of alkyl radicals to unsaturated systems:

Unsaturated systems with polar substituents can yield carbon-centered adduct radicals that react as donors or acceptors in reaction 1 and 2.

Scheme III. Addition-Elimination Mechanism



When the unsaturated radicophile is an anion, the resulting adduct is a radical anion. This radical anion readily transfers an electron to alkylmercury halide to regenerate alkyl radical by a process referred to as S_{RN} substitution (Scheme IV).[18,19,25,27]

Carbon-centered acceptor radicals, which can be formed by the addition of an alkyl radical to an electron poor alkene, will react with alkylmercury halide by S_H2 substitution at Hg. For some carbon-centered radicals, such as enolyl-type radicals, this process is inefficient. In these cases, addition of an easily oxidized anion, such as I^-, can result in an efficient chain process by formation of an ate-complex (see Chapter I).

Scheme IV. Addition to Unsaturated Anion

$$R^{\bullet} + Nu^{-} \longrightarrow RNu^{\bullet -}$$

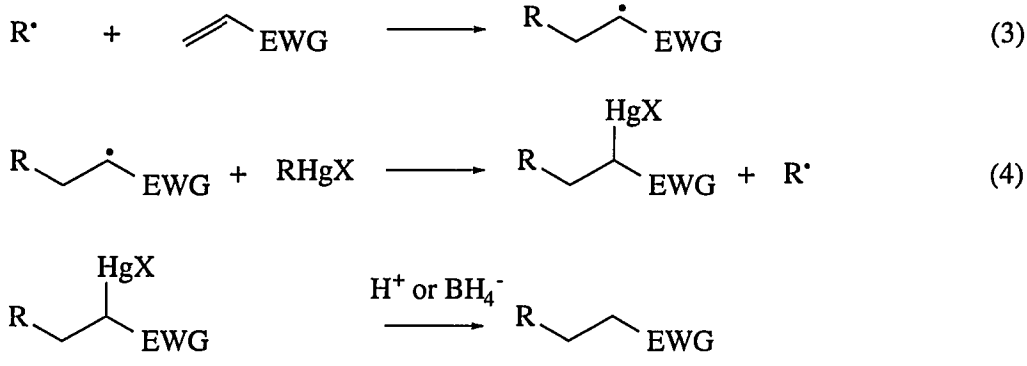
$$RNu^{\bullet -} + RHgX \longrightarrow RNu + R^{\bullet} + Hg^{0} + X^{-}$$

CHAPTER I. REDUCTIVE RADICAL ALKYLATIONS OF SUBSTITUTED OLEFINS BY ALKYLMERCURY HALIDES

A. Photostimulated Reductive Alkylations of Alkenes

Alkenes substituted with electron withdrawing groups undergo reductive alkylation when they are photolyzed with alkylmercury halides. The reaction is recognized to occur for either CH_2=$CHSO_2Ph$ or CH_2=$CHP(O)(OEt)_2$ via the intermediate organomercurials (Scheme V).[24]

Scheme V. Addition to the Electron-Poor Olefin



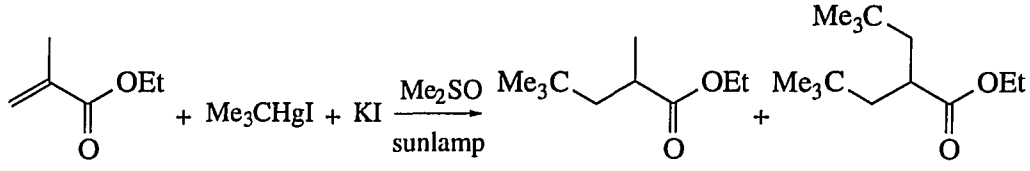
Reductive alkylations of α, β-unsaturated carbonyls or nitriles do not occur readily via Scheme V. However, in the presence of iodide salts efficient reductive alkylations occur for α,β-unsaturated carbonyls that can form secondary-enolyl radicals in reaction 3. It has been suggested that reaction 5 now occurs.[34]

$$RCH_2C^{\bullet}HC(=O)X + RHgI_2^- \longrightarrow RCH_2CH=C(O^-)X + R^{\bullet} + HgI_2 \qquad (5)$$

The addition of I^- to solutions of a Me_3CHgCl forms Me_3CHgI, ate-complexes such as $Me_3CHg(Cl)(I)^-$ and $Me_3CHgI_2^-$, and possibly $(Me_3C)_2Hg$ via comproportionation. The photostimulated or thermal rate of formation of alkyl radicals is greatly accelerated by the addition of iodide salts to alkylmercury halides because of the increased photolability of species such as RHgI, $RHgX_2^-$, and R_2Hg.[35] Reaction 5 may also occur more readily with Me_3CHgI than with Me_3CHgCl. In addition, when reaction 4 or 5 do not occur readily, it is possible that hydrogen atom transfer from Me_3CHgX to the adduct radical (reaction 6) may occur more readily for Me_3CHgI than for Me_3CHgCl.

$$RCH_2CH(EWG)^{\bullet} + Me_3CHgX \longrightarrow RCH_2CH_2(EWG) + Me_2C{=}CH_2 + HgX^{\bullet} \qquad (6)$$

Table I. *tert*-Butylation of Ethyl Methacrylate with Me_3CHgI/KI[a]



1 4 4 **1** **2**

Entry	Time (h)	Yield, %[b]	
		1	**2**
1	1	18	2
2	2	29	7
3	4	23	13
4	6	25	14
5	8	28	15
6	10	29	15
7	12	27	17

[a]Reaction of 0.25 mmol of ethyl methacrylate with 4 equiv. of Me_3CHgI and 4 equiv. of KI in 5 mL solvent with 275 W fluorescent sunlamp irradiation at *ca.* 35 °C.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

In an effort to study substituent effects on the reactivities of substituted olefins toward alkyl radical addition, ethyl methacrylate was reacted with the *tert*-butyl radical generated photochemically from the alkylmercurial. The photostimulated process failed to give a simple reaction for the *tert*-enolyl radical. Both mono- and di-*tert*-butylation products were obtained (Table I and Figure I), presumably because of the disproportionation of the initial adduct radical followed by further *tert*-butylation.

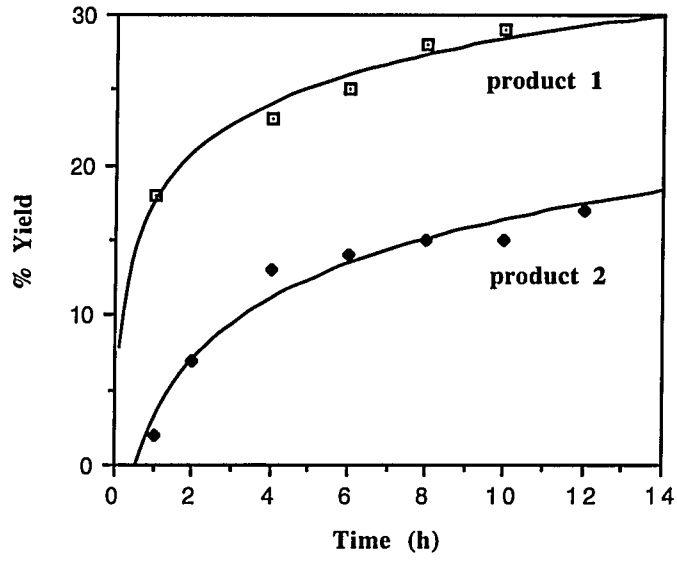


Figure I. Yields of Product **1** and **2** versus Reaction Time

A mechanism which accounts for the experimental observations involves a *tert*-butyl radical attack on ethyl methacrylate followed by either ate-complex reduction of the adduct radical or the disproportionation of the adduct radical. The disproportionation of the initial adduct radical produces a reductive mono-*tert*-butylation product as well as another alkene which is as reactive as the starting alkene for the radical addition. Further *tert*-

butylation of this newly formed alkene gives the di-*tert*-butylation adduct radical which yields the reductive di-*tert*-butylation product upon ate-complex reduction (Scheme VI).

Apparently, the ate-complex is not totally ineffective toward the tertiary enolyl radical. However, the initial adduct radical readily undergoes disproportionation by transfer of the hydrogen from the methyl group adjacent to the radical center. No oxidative di-*tert*-butylation product was ever observed under these conditions, probably because of the steric hindrance for the disproportionation of $(Me_3CCH_2)_2CCO_2Et^{\bullet}$.

Scheme VI. Mechanism of Photostimulated *tert*-Butylation of Ethyl Methacrylate

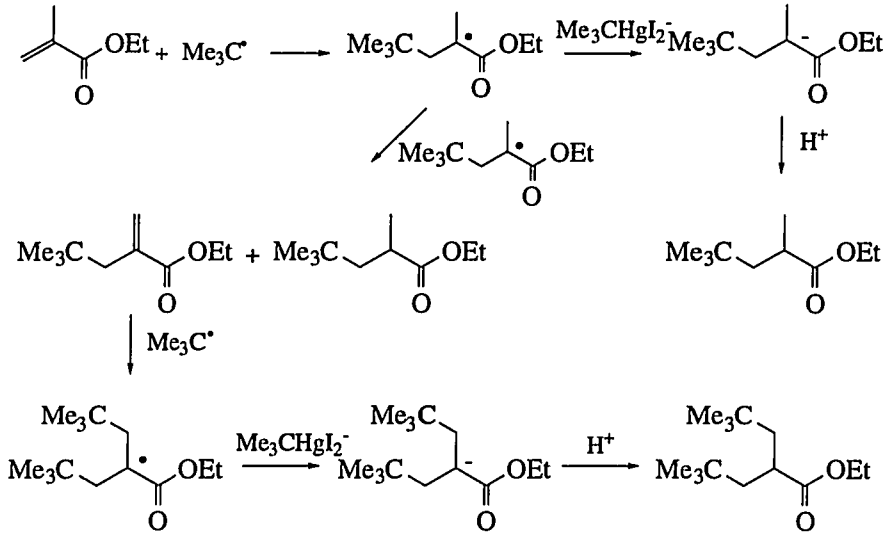
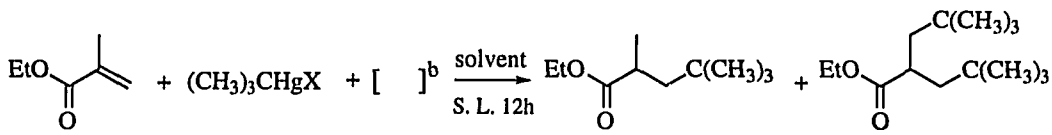


Table II summarizes experiments using 1,4-diaza[2.2.2]bicyclooctane (DABCO) and Et_3N as possible hydrogen donors. Although increases in the ratio of **1/2** were observed with 4 equiv. of the amines, the effects were small. Even when Et_3N was employed as 25 vol.% of the solvent the ratio of **1/2** was not increased, for example, compare entry 3 (**1/2** = 4.6) to entry 8 (**1/2** = 3).

Table II. Photostimulated *tert*-Butylation of Ethyl Methacrylate[a]



1 **2**

Entry	X	Molar Equivalent			Solvent	Yield, %[c]	
		KI	DABCO	Et_3N		**1**	**2**
1	Cl	4			Me_2SO	18	13
2	Cl	4	4		Me_2SO	19	10
3	Cl	8			Me_2SO	28	6
4	Cl	8	4		Me_2SO	26	14
5	Cl	8		4	Me_2SO	17	8
6	I				Me_2SO	10	10
7	I	8			Me_2SO	22	16
8	Cl	8			Me_2SO/Et_3N 3:1[d]	35	12
9	I	4			Me_2SO/Et_3N 3:1[d]	31	15

[a]Reaction of 0.25 mmol of ethyl methacrylate with 4 equiv. of Me_3CHgX and other reagents in 5 mL solvent with 275 W fluorescent sunlamp irradiation at *ca.* 35 °C.
[b]Symbol [ ] means added reagents whose molar equivalent is defined in the table.
[c]By GC and ^1H NMR integration with toluene (0.1 mmol) as an internal standard.
[d]Ratio by volume.

Dialkylation in the photostimulated alkylation of ethyl methacrylate complicated the measurement of relative reactivities in competition reactions. In order to obtain a single alkylation product, a better hydrogen donor than the adduct radical has to be provided to prevent the disproportionation from occurring.

B. Reductive Alkylation in the Presence of A Hydrogen Donor

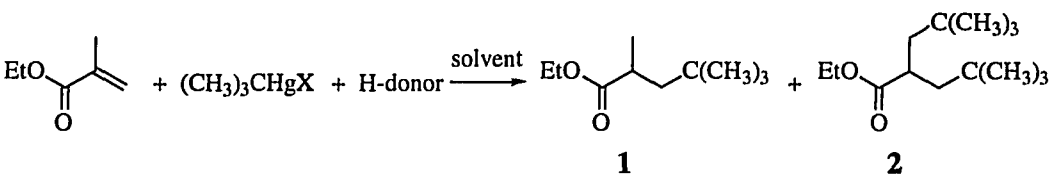
Giese has described many examples of the reductive alkylation of olefins upon reaction with alkylmercury halides and sodium borohydride in methylene chloride and aqueous sodium hydroxide mixture. The Giese process is believed to involve the reactive intermediate alkylmercury hydride (RHgH) as a reaction initiator and hydrogen atom transfer agent in a free radical chain process (Scheme I). Alkylmercury hydride generated with alkaline sodium borohydride has the drawback that alkylmercury hydrides are better hydrogen atom donors than are tin hydrides. Thus it becomes difficult for intermolecular addition of an alkyl radical to compete with direct reduction of the alkyl radical.[36] Therefore, an excess of the alkene (as much as 30 equiv.) is usually required.

Silyl hydrides are rather poor hydrogen atom donors toward alkyl radicals[37] and therefore do not support chain reactions under normal conditions. However, my experimental results demonstrate that silyl hydrides can be excellent reagents for use in conjunction with alkylmercury halides for the reductive radical alkylation of electron-poor olefins in Me_2SO solution (Table III).

The results summarized in Table III demonstrate that triethylsilane is an excellent reagent for use in conjunction with alkylmercury halides. The results also confirmed the idea that hydrogen donation can change the product distribution observed from an adduct radical such as $Me_3CCH_2C(Me)COOEt^{\bullet}$. The product distribution of this substrate can be used as a diagnostic criterion for hydrogen atom donation. The reason that the silyl hydride has been ignored for this system in the past is that silyl hydride is, in fact, quite unreactive as a hydrogen donor towards alkyl radicals.[38] Nevertheless, experimental results suggested that it does donate hydrogen atoms when used in conjunction with RHgX in Me_2SO. The system also slowly forms alkyl radicals at room temperature. The slow

formation of alkyl radicals combined with an appropriate rate of donation of hydrogen atoms appear to be the main reasons for the favorable results observed. The silyl hydride method has also been tested in other solvents such as methylene chloride, benzene, THF, and acetonitrile. No reaction has ever been observed in those solvents. Reaction does occur in DMF but gives very poor yield.

Table III. *tert*-Butylation of Ethyl Methacrylate in the Presence of Hydrogen Donors[a]



1 **2**

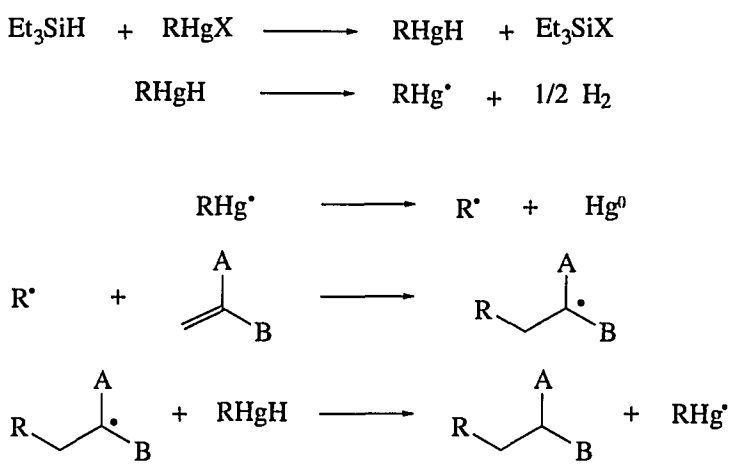
Entry	X	H-donor[a]	Solvent	Time	Yield, %[b]	
					1	**2**
1	I	HCO_2NH_4	Me_2SO	1 h	22	1
2	I	*n*-Bu_3SnH	Me_2SO	10 min	67	0
3	Cl	*n*-Bu_3SnH	Me_2SO	10 min	50	0
4	Cl	$NaBH_4/OH^-$	CH_2Cl_2	20 min	60	0
5	Cl	Et_3SiH	Me_2SO	hυ, 11 h	90	0
6	Cl	Et_3SiH	Me_2SO	11 h	93	0

[a]Reaction of 0.25 mmol of ethyl methacrylate with 2 equiv. of Me_3CHgX and hydrogen donor in 5 mL solvent with or without 275 W fluorescent sunlamp irradiation at *ca.* 35 °C.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

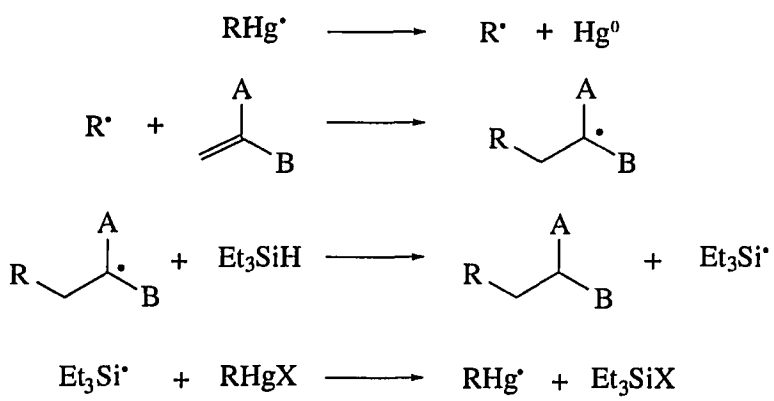
The mechanism of this alkylation reaction has been investigated by several kinetic methods. The kinetic chain length (k.c.l.; for detailed discussion refer to chapter II) has been measured by the di-*tert*-butyl nitroxide inhibition method for the reaction of 2 equivalents of Me_3CHgCl and triethylsilane with 0.1 M ethyl methacrylate. The initial k.c.l. was found to be 8 for this substrate. Furthermore, when 5-hexenylmercury bromide

was reacted with ethyl acrylate, ethyl 4-cyclopentylbutyrate was obtained as the major product. The structure of the observed product was verified by comparison of proton NMR, MS, and GC data with that of the product formed from the reaction of cyclopentyl-carbinylmercury chloride with ethyl acrylate. These experiments require that the reaction is a free radical chain reaction. Two possible mechanisms (Schemes VII and VIII) are proposed as follows:

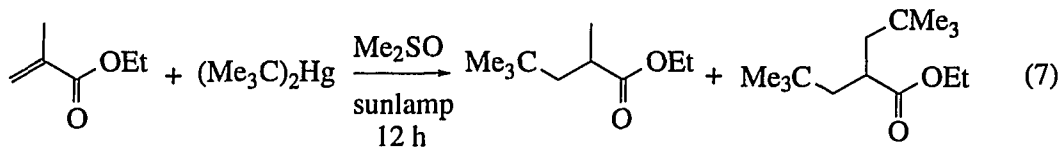
Scheme VII. Mechanism involved with the RHgH



Scheme VIII. Mechanism involved with the Silyl Radical (propagation steps)

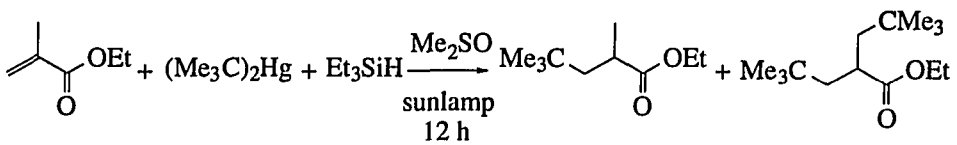


Experimental evidence suggests that triethylsilyl radical is not the major chain carrier (Scheme VIII) and that the reaction involves alkylmercury hydride as an intermediate (Scheme VII). The reaction of Me_3CHgCl with Et_3SiH was monitored by ^1H NMR in d_6-Me_2SO to follow the consumption of Et_3SiH. Addition of $(Me_3C)_2NO^{\bullet}$ had no effect on this reaction. Furthermore, addition of Et_3SiH to a known radical reaction does not change the product distribution. Therefore, the direct hydrogen donation from Et_3SiH to the adduct radical is at most a minor reaction pathway. Thus, radical *tert*-butylation of ethyl methacrylate with irradiation of di-*tert*-butylmercury give 14% of the mono-*tert*-butylation product and 12% of di-*tert*-butylation product (reaction 7). The product ratio does not change much in the presence of four equivalent of triethylsilane (reaction 8). The yields of **1** and **2** in reaction 8 are similar to those observed for the photostimulated reaction with *tert*-butylmercury chloride in the presence of potassium iodide (reaction 9).



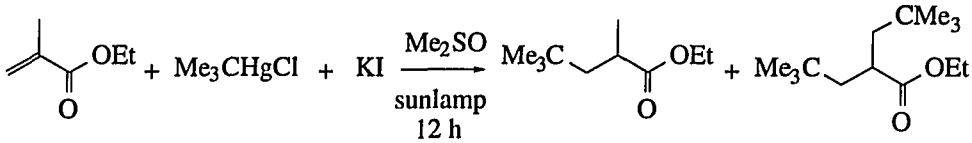
(7)

1 4 14% 12%



(8)

1 4 4 18% 13%



(9)

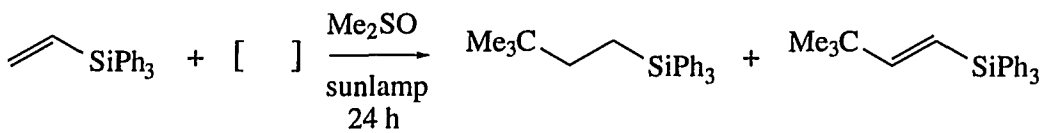
1 4 4 18% 13%

C. Radical Alkylations Promoted by Silyl Hydrides

1. Radical Alkylation of Triphenylvinylsilane

Photostimulated reactions of alkylmercury halides with triphenylvinylsilane produce both reductive and oxidative alkylation products. Results summarized in Table IV demonstrated that the ate-complex is not effective for the conversion of the adduct radical to the reductive alkylation product **4**, nor is base effective for the preferential formation of the oxidative alkylation product **5**.

Table IV. Photostimulated Radical *tert*-Butylation[a]



3 **4** **5**

Entry	X	Molar Equivalent				Yield, %[b]		
		Me_3CHgX	KI	DABCO	Et_3N	**3**	**4**	**5**
1	Cl	3				6	13	
2	Cl	3	6			15	20	15
3	Cl	3	12			8	22	20
4	I	3					56	2
5	I	3	3				20	15
6	I	3	6				36	28
7	I	3		3			58	3
8	I	3			3		58	3

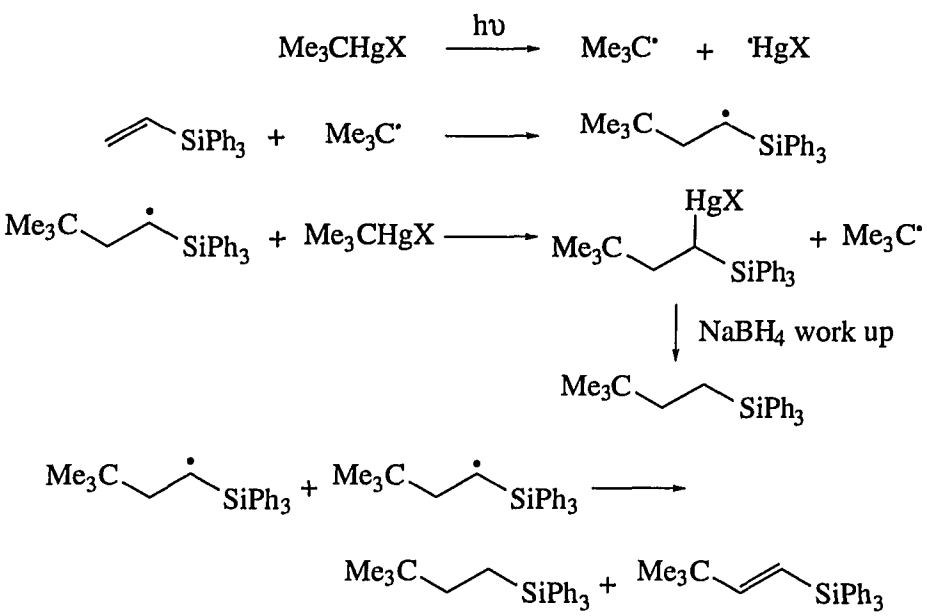
[a]Reaction of 0.2 mmol with 3 equiv. of Me_3CHgX in 5 mL of Me_2SO with 275 W fluorescent sunlamp irradiation at *ca.* 35 °C followed by the $NaBH_4$ work up.

[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

Photolysis with *tert*-butylmercury chloride forms mainly reductive alkylation product **4** in very low yield. With *tert*-butylmercury iodide photolysis again yields mainly product **4** but in considerable higher yield. However, the same reaction only yielded small amount of product **4** (5%) and **5** (2%) when it was worked up with sodium thiosulfate solution. Instead, 70% of 3,3-dimethyl-1-triphenylsilylbutylmercuric iodide was observed by crude NMR spectrum. Mixtures of *tert*-butylmercury chloride and KI or *tert*-butylmercury iodide and KI under similar photolysis conditions form a mixture of the disproportionation products.

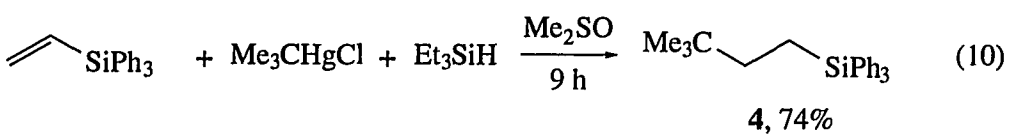
The mechanism proposed is *tert*-butyl radical attack upon olefin to give adduct radical followed by displacement of *tert*-butyl radical propagating the chain. The saturated product is obtained by work up with $NaBH_4$. The unsaturated product could be formed by disproportionation (Scheme IX).

Scheme IX. Mechanism for Photochemical Reaction



The reaction products with this alkene seem to be controlled by the rate of photodissociation of the adduct mercurial 3,3-dimethyl-1-triphenylsilylbutylmercuric halide. Thus, at low rate of photodissociation in the absence of KI the adduct mercurials are mainly converted to the reductive alkylation product upon $NaBH_4$ work up. In the presence of added KI a much faster photodissociation occurs, possibly by the photolysis of the ate-complexes or the very labile symmetrization product $(Me_3C)_2Hg$. Now a high concentration of the adduct radical is formed and products result from a bimolecular disproportionation process. In addition, the further photolysis of the adduct mercurial in the presence of added KI regenerates the adduct radical and eventually leads to disproportionation products.

The reaction of triphenylvinylsilane with *tert*-butylmercury chloride (4 equiv.) in the presence of triethylsilane (4 equiv.) in the dark gives only the reductive *tert*-butylation product in good yield (reaction 10).

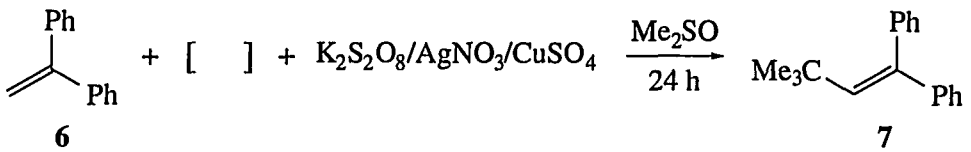


4, 74% (10)

2. Radical *tert*-Butylations of 1,1-Diphenylethylene

The photostimulated radical *tert*-butylation of 1,1-diphenylethylene in the presence of $K_2S_2O_8/Ag^+/Cu^{+2}$ gives the only oxidative product (Table V). Again, the ate-complex is not effective in reducing the adduct radical and no reductive tert-butylation product is ever observed. Under the best conditions (entry 6) a 10-fold excess of *tert*-butylmercury iodide was required to give a 50% yield of **7**.

Table V. Photostimulated Radical *tert*-Butylation of $(Ph)_2C=CH_2$[a]

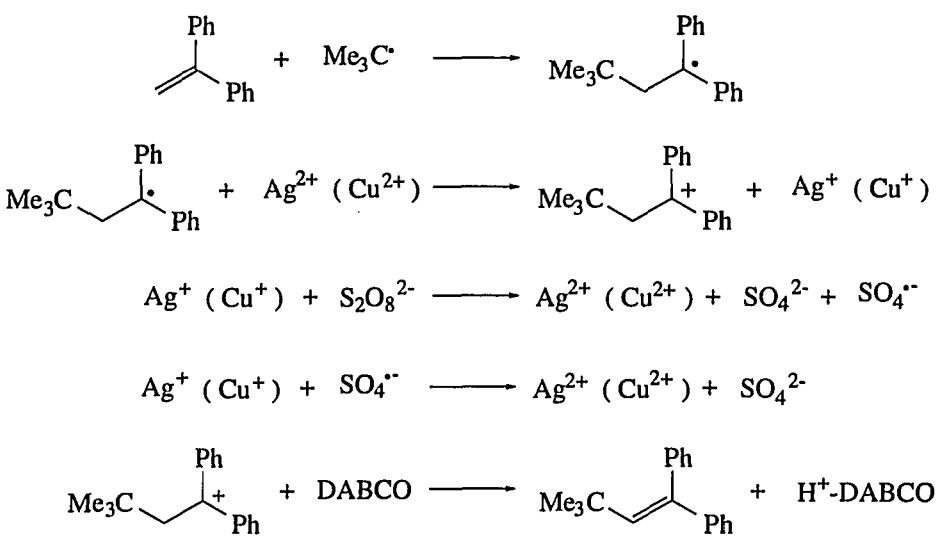


6 **7**

Entry	Molar Equivalent			Yield, %[b]	
	Me_3CHgI	KI	DABCO	**6**	**7**
1	3			12	18
2	3	3		3	19
3	3		2	0.5	25
4	3	3	2	0.3	10
5	5		2.5	5	43
6	10		5	4	50

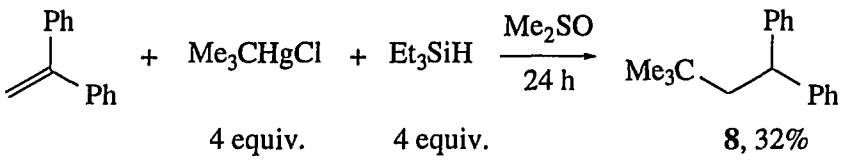
[a]Reaction of 0.2 mmol of $(Ph)_2C=CH_2$ with 2 equiv. of $K_2S_2O_8$, 0.2 equiv. of $AgNO_3$, 0.05 equiv. of $CuSO_4$, and other reagents in 5 mL of Me_2SO with 275 W fluorescent sunlamp irradiation at *ca.* 35 °C. [b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

Scheme X. Mechanism of Oxidative Alkylation of 1,1-Diphenylethylene



The mechanism of the reaction appears to involve *tert*-butyl radical attack on the alkene to give an adduct radical which is then oxidized to the adduct cation by catalytic amounts of Ag^{2+} or Cu^{2+}. Deprotonation of the adduct cation by a base gives the oxidative alkylation product. Persulfate is consumed to recycle the oxidizing agent (Scheme X).[39]

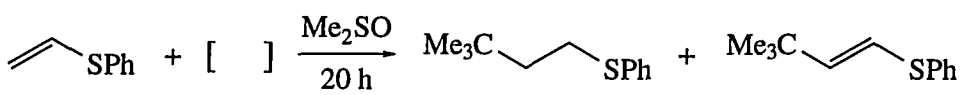
The radical alkylation of 1,1-diphenylethylene with the silane system gives the reductive alkylation product as the only observed product (reaction 11). However, the yield is poor (32%).



4 equiv. 4 equiv. **8**, 32% (11)

3. Radical *tert*-Butylation of Vinyl Phenyl Sulfide

Table VI. Photochemical *tert*-Butylation of Vinyl Phenyl Sulfide[a]



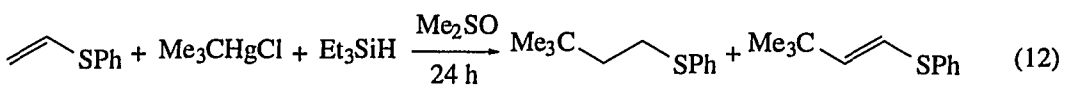
9 **10**

Entry	X	Molar Equivalent					Yield, %[b]	
		Me_3CHgX	$K_2S_2O_8$	$AgNO_3$	$CuSO_4$	DABCO	**9**	**10**
1	I	3					trace	8
2	Cl	5	2	0.2	0.05	1	12	8
3	I	5	2	0.2	0.05	1	12	15

[a]Reaction of 0.2 mmol of vinyl phenyl sulfide with reagents in 5 mL of Me_2SO with 275 W fluorescent sunlamp irradiation at *ca.* 35 °C.
[b]By GC and ^1H NMR integration with toluene as an added internal standard.

With vinyl phenyl sulfide, photostimulated reaction with *tert*-butylmercury iodide gives a low yield of a mixture of the reductive and oxidative alkylation products (Table VI). Apparently the sulfur substituent group does not promote the oxidation of the adduct radical by Ag^{2+} or Cu^{2+}. The observed products are formed by disproportionation with a considerable amount of polymeric product observed.

In the presence of a silyl hydride, the *tert*-butylation reaction of vinyl phenyl sulfide gives the reductive product as the major product in a fair yield. However, the alkene expected from the disproportionation of the adduct radical is also observed (reaction 12).



(12)

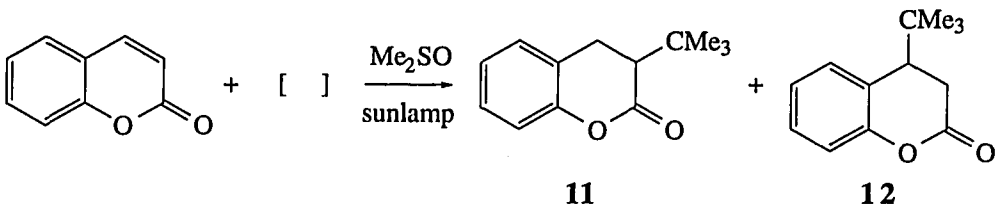
4 equiv. 4 equiv. **9**, 52% **10**, 5%

4. Radical *tert*-Butylation of Coumarin

The *tert*-butylation of coumarin with *tert*-butylmercury chloride in the presence of triethylsilane gives 3- and 4-*tert*-butylation products (**11** and **12**).

The results summarized in Table VII indicate that the radical *tert*-butylation of coumarin is reversible. At low RHgH steady state concentration, i.e. low Et_3SiH concentration, about equal amounts of reductive alkylation occurs at C-3 and C-4. However, at high Et_3SiH concentration, compound **11** greatly predominates indicating that attack at C-3 is kinetically preferred. Comparison of entries 4 and 5 also suggests that **11** is thermodynamically preferred to **12.**

Table VII. Reductive *tert*-Butylation of Coumarin[a]



11 **12**

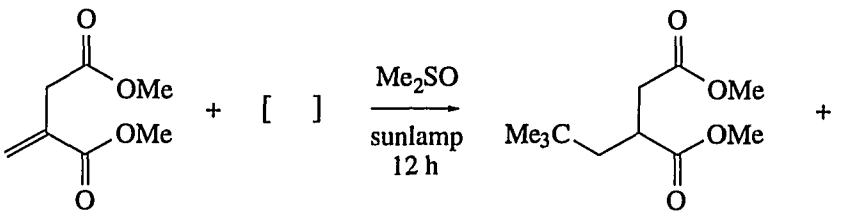
Entry	Molar Equivalent		Time (h)	Yield, %[b]	
	Me_3CHgCl	Et_3SiH		**11**	**12**
1	4	0.4	24	6	6
2	4	1	24	13	6
3	4	2	24	16	10
4	4	4	12	40	8
5	4	4	24	55	2

[a]Reaction of 0.25 mmol of coumarin with 4 equiv. of Me_3CHgCl in 5 mL of Me_2SO followed by addition of Et_3SiH with 275 W fluorescent sunlamp irradiation at *ca.* 35 °C.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

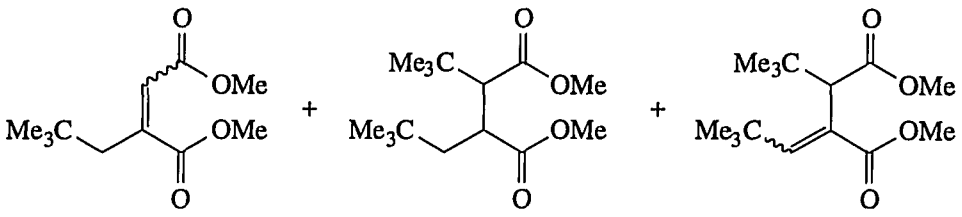
5. Radical *tert*-Butylation of Dimethyl Itaconate

The silyl hydride method gives only the monoalkylation product even in cases where the loss of hydrogen is favorable. In entry 9 of Table VIII, dimethyl itaconate gives only the mono-*tert*-butylation product and di-*tert*-butylation is not observed in the presence of triethylsilane. When one equivalent of *tert*-butylmercury iodide is used in the presence of a base, the oxidative *tert*-butylation product (**15**) can be preferentially formed (entries 1, 2, and 3). When an excess of the alkylmercurial is used, further alkylation is observed. Under these forcing conditions where a base is used, the oxidative di-*tert*-butylation product is also observed (entries 6, 7, and 8), but the major product is the reductive di-*tert*-butylation product **16** formed by addition of *tert*-butyl radical to **15**.

Table VIII. Radical *tert*-Butylations of Dimethyl Itaconate[a]



13 **14**



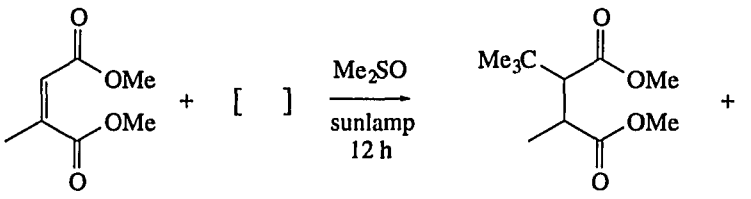
15 **16** **17**

Entry	X	Molar Equivalent					Yield, %[b]				
		Me_3CHgX	KI	DABCO	DBU	Et_3SiH	**13**	**14**	**15**	**16**	**17**
1	I	1.2	1.2	1.2			4		52	10	
2	I	1		1.5			10		56	6	
3	I	1			2		3		38	7	
4	I	4					7	13		3	
5	I	4	4				14	18		3	
6	I	4	4	4						52	18
7	I	4			4					53	13
8	I	4		4						46	18
9	Cl	4				4		88			

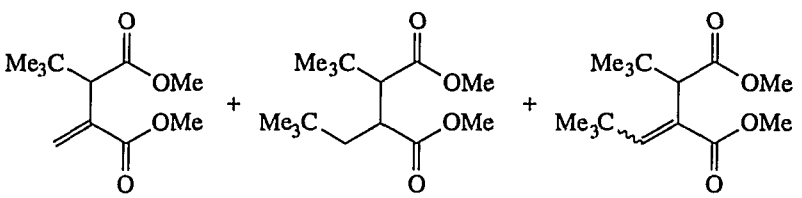
[a]Reaction of 0.1 mmol of dimethyl itaconate with Me_3CHgX and other reagents in 4 mL of Me_2SO with 275 W fluorescent sunlamp irradiation at *ca.* 35 °C.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

6. Radical *tert*-Butylation of Dimethyl Citraconate and Other 1,2-Disubstituted Alkenes

Table IX. Radical *tert*-Butylation of Dimethyl Citraconate[a]



18 **19**



20 **16** **17**

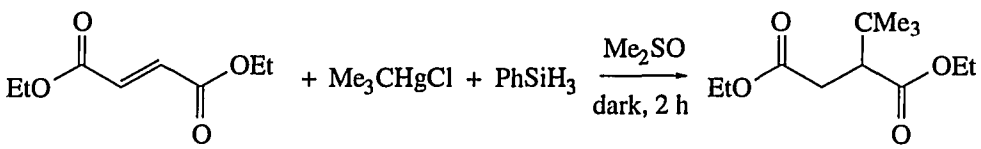
Entry	X	Molar Equivalent			Yield, %				
		Me_3CHgX	DABCO	Et_3SiH	**18**	**19**	**20**	**16**	**17**
1	Cl	4		4	11	60		8	3
2	I	1.2	4		43	5	5	14	3
3	I	4	4		16	15		28	9

[a]Reaction of 0.1 mmol of dimethyl citraconate with Me_3CHgX and other reagents in 4 mL of Me_2SO with 275 W fluorescent sunlamp irradiation at *ca.* 35 °C.
[b]By GC and ^1H NMR integration with toluene as an added internal standard.

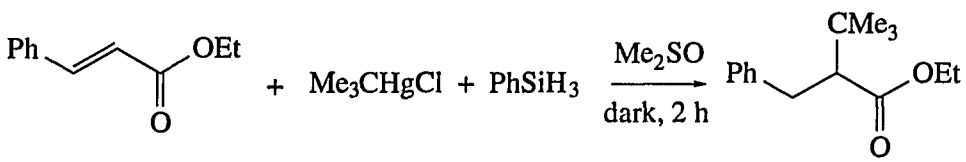
Reactions of *tert*-butylmercury chloride in the presence of hydrides with 1, 2-disubstituted alkenes are often ineffective unless both substituents are electron withdrawing. Coumarin, with its low steric requirements is an exception. Dimethyl citraconate forms **19** in 60% yield in the presence of Et_3SiH. A small amount of di-*tert*-butylation products (**16** and **17**) are observed. These apparently result from disproportionation of the

initial adduct radical to form **19** and **20**. Attack of *tert*-butyl radical upon **20** leads to **16** and isomers of **17**. With 1.2 equiv. of *tert*-butylmercury iodide in the presence of DABCO, **20** can be observed although the major product is still **16** (Table IX).

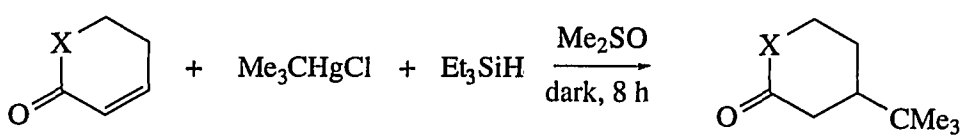
1,2-Disubstituted alkenes such as diethyl fumarate and maleate give the *tert*-butylation products in very good yield in the presence of silanes or I^- under irradiation. However, ethyl *trans*-cinnamate, 5,6-dihydro-2*H*-pyran-2-one, or 2-cyclohexenone give low yield and chalcone fails to react at all (reaction 13-16), although all these substrates give fair to good yield of alkylation product in the presence of I^- under irradiation.



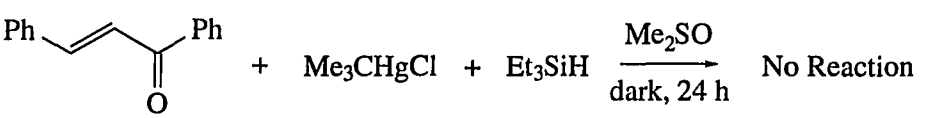
4 equiv. 4 equiv. 84% (13)



4 equiv. 4 equiv. 18% (14)



X = O, CH_2 4 equiv. 4 equiv. X = O, 20%; X = CH_2, 22% (15)

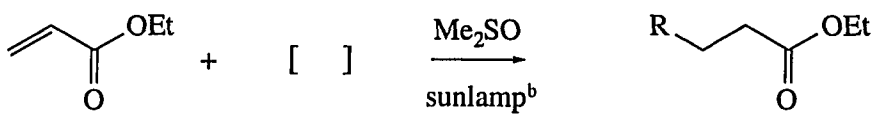


4 equiv. 4 equiv. (16)

7. Radical Alkylation of Ethyl Acrylate and α-Substituted Ethyl Acrylates

The radical alkylation of ethyl acrylate gives the reductive addition product as the only observed product either photochemically in the presence of KI or in the presence of a silyl hydride in the dark (Table X). Photolysis had no effect on the silane promoted reactions.

Table X. Radical Alkylations of Ethyl Acrylate[a]



21, R = *t*-Bu
22, R = *n*-Bu

Entry	R	Molar Equivalent				Time (h)	Yield,[c] % (Prdt)	
		RHgCl	KI	Et_3SiH	$PhSiH_3$			
1	*t*-Bu	4	8			12	73	(**21**)
2	*t*-Bu	4		4		12	84	(**21**)
3	*t*-Bu	4			4	1	88	(**21**)
4	*n*-Bu	2		2		12	34	(**22**)
5	*n*-Bu	4		4		13	64	(**22**)
6	*n*-Bu	4	4	4		14	93	(**22**)
7	*n*-Bu	4			4	14	12	(**22**)
8	*n*-Bu	4	4		4	20	10	(**22**)

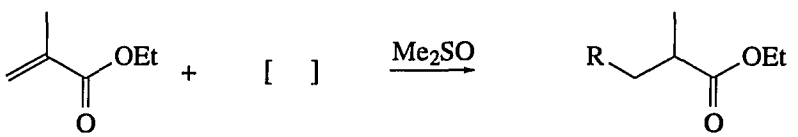
[a]Reaction of 0.1 mmol of ethyl acrylate with 4 equiv. of RHgX and other reagents in 4 mL of Me_2SO with or without 275 W fluorescent sunlamp irradiation at *ca.* 35 °C.
[b]Photolysis with the sunlamp has no effect on the reactions utilizing silanes.
[c]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

Photostimulated *tert*-butylation of ethyl methacrylate with *tert*-butylmercury chloride and KI gives a mixture of mono- and di-*tert*-butylation products (Table II). With 2 equivalents of *tert*-BuHgCl/Et_3SiH, ethyl methacrylate gives a single *tert*-butylation product in excellent yield (Table XI). With *tert*-BuHgCl/$PhSiH_3$, 4 equivalents of reagents have to be used to obtain a fair yield. For *n*-BuHgCl/Et_3SiH reaction, KI must be used to produce *n*-butylation product in good yield. With *n*-BuHgCl/$PhSiH_3$, the reaction still gives low yield despite the apparently fast consumption of the mercurial.

tert-Butylations of ethyl α-phenylacrylate with the silane system give fair to good yield. On the other hand, *n*-butylations give poor alkylation yields due to the polymerization of the starting material (Table XII).

Excellent yield could be obtained with either triethylsilane or phenylsilane for *tert*-butylation and *n*-butylation of ethyl α-chloroacrylate[40] (Table XIII).

Table XI. Radical Alkylations of Ethyl Methacrylate[a]

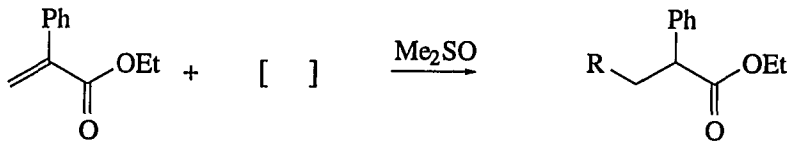


1, R = *t*-Bu
23, R = *n*-Bu

Entry	R	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)	
		RHgCl	KI	Et_3SiH	$PhSiH_3$			
1	*t*-Bu	2		2		11	93	(**1**)
2	*t*-Bu	4			4	1	54	(**1**)
3	*n*-Bu	2		2		12	30	(**23**)
4	*n*-Bu	4	2	4		20	74	(**23**)
5	*n*-Bu	4			4	2	10	(**23**)

[a]Reaction of 0.1 mmol of ethyl methacrylate with RHgCl and other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

Table XII. Radical Alkylations of Ethyl α-Phenylacrylate[a]

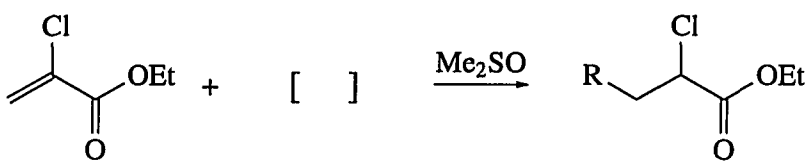


24, R = *t*-Bu
25, R = *n*-Bu

Entry	R	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)	
		RHgCl	KI	Et_3SiH	$PhSiH_3$			
1	*t*-Bu	4		4		8	73	(**24**)
2	*t*-Bu	4			4	8	78	(**24**)
3	*n*-Bu	4	2	4		12	41	(**25**)
4	*n*-Bu	4			4	9	13	(**25**)

[a]Reaction of 0.1 mmol of ethyl α-phenylacrylate with RHgCl and other reagents in 4 mL of Me_2SO
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

Table XIII. Radical Alkylations of Ethyl α-Chloroacrylate[a]



26, R = *t*-Bu
27, R = *n*-Bu

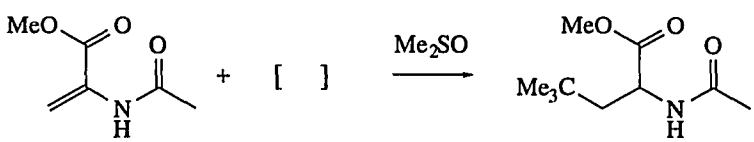
Entry	R	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)	
		RHgCl	KI	Et_3SiH	$PhSiH_3$			
1	*t*-Bu	4		4		10	85	(**26**)
2	*t*-Bu	4			4	10	95	(**26**)
3	*n*-Bu	4	4	4		8	85	(**27**)
4	*n*-Bu	4			4	7	93	(**27**)

[a]Reaction of 0.1 mmol of ethyl α-chloroacrylate with RHgCl and other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

8. Radical *tert*-Butylation of Methyl 2-Acetamidoacrylate

With the silyl hydride system, *tert*-butylations of methyl 2-acetamidoacrylate give the reductive alkylation product as the only observed product (Table XIV). Photostimulated reaction with *tert*-butylmercury chloride and KI gives two products through disproportionation of the adduct radicals with amidyl hydrogen atom transfer.

Table XIV. *tert*-Butylations of Methyl 2-Acetamidoacrylate[a]



28

Entry	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)	
	Me_3CHgCl	KI	Et_3SiH	$PhSiH_3$			
1	4	4			hυ, 9	25[c]	(**28**)
2	4		4		2	48	(**28**)
3	4			4	2	55	(**28**)

[a]Reaction of 0.1 mmol of methyl 2-acetamidoacrylate with Me_3CHgCl and other reagents in 4 mL of Me_2SO.

[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

[c]For photostimulated reaction, 16% of oxidative alkylation product was observed due to the hydrogen atom donation from the amidyl group.

9. Radical Alkylation of Acrylonitrile and α-Substituted Acrylonitrile

Radical *tert*-butylations of acrylonitrile give excellent yield in the presence of either triethylsilane or phenylsilane. With phenylsilane, the reaction is complete within one hour. *n*-Butylation in the presence of Et_3SiH gives better yield than that with $PhSiH_3$ indicating that a better yield is produced by the slow formation of *n*-BuHgH (Table XV).

Table XV. Radical Alkylations of Acrylonitrile[a]

29, R = *t*-Bu
30, R = *n*-Bu

Entry	R	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)	
		RHgCl	KI	Et_3SiH	$PhSiH_3$			
1	*t*-Bu	4		4		12	90	(**29**)
2	*t*-Bu	4			4	1	95	(**29**)
3	*n*-Bu	4	2	4		20	73	(**30**)
4	*n*-Bu	4			4	12	50	(**30**)

[a]Reaction of 0.1 mmol of acrylonitrile with 4 equiv. of RHgCl and other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

Table XVI. Radical Alkylation of Methacrylonitrile[a]

31, R = *t*-Bu
32, R = *n*-Bu

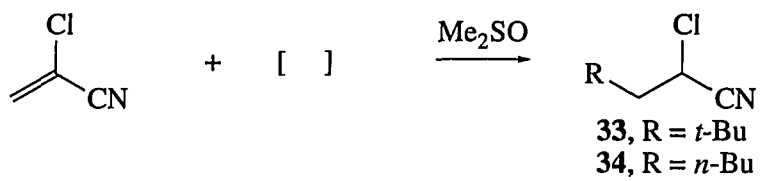
Entry	R	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)	
		RHgCl	KI	Et_3SiH	$PhSiH_3$			
1	*t*-Bu	4		4		22	86	(**31**)
2	*t*-Bu	4			4	3	40	(**31**)
3	*n*-Bu	4	2	4		20	86	(**32**)
4	*n*-Bu	4			4	24	11	(**32**)

[a]Reaction of 0.1 mmol of methacrylonitrile with 4 equiv. of RHgCl and other reagents in 4 mL of Me_2SO
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

Radical alkylation of methacrylonitrile with triethylsilane gives very good yield with either *tert*-butylmercury chloride or *n*-butylmercury chloride (Table XVI). Faster reactions with phenylsilane give low yield with both mercurials (entries 2 and 4).

Radical alkylation of 2-chloroacrylonitrile with either triethylsilane or phenylsilane provide good yield (Table XVII). Faster reactions with phenylsilane give slightly higher yield than the slower reactions with triethylsilane. Since 2-chloroacrylonitrile is a very reactive alkene towards alkyl radicals, the yield of the reductive alkylation product is not controlled by the rate of generation or steady state concentration of alkylmercury hydride.

Table XVII. Radical Alkylations of 2-Chloroacrylonitrile[a]



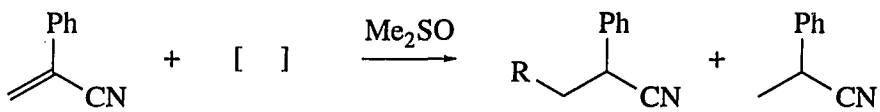
33, R = *t*-Bu
34, R = *n*-Bu

Entry	R	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)	
		RHgCl	KI	Et_3SiH	$PhSiH_3$			
1	*t*-Bu	4		4		12	76	(**33**)
2	*t*-Bu	4			4	1	85	(**33**)
3	*n*-Bu	4	2	4		20	82	(**34**)
4	*n*-Bu	4			4	1	86	(**34**)

[a]Reaction of 0.1 mmol of 2-chloroacrylonitrile with 4 equiv. of RHgCl and other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

Attempted alkylation of atroponitrile[41] with the silane system was not very successful (Table XVIII) for two reasons. First of all, atroponitrile is very susceptible to polymerization. Secondly, direct reduction of the alkene by the silyl hydride in the presence of the mercurial was a major side reaction.

Table XVIII. Radical Alkylations of atroponitrile[a]



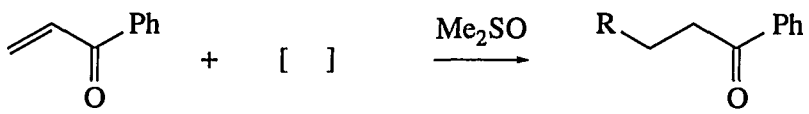
Entry	R	X	Molar Equivalent			Time (h)	Yield, %[b]	
			RHgX	Et_3SiH	$PhSiH_3$			
1	*t*-Bu	Cl	4	4		12	15,	15
2	*t*-Bu	Cl	4		4	3	25,	29
3	*t*-Bu	I	4	4		10	13,	17
4	*n*-Bu	I	4	4		10	24,	24
5	*n*-Bu	Cl	4		4	4	19,	30

[a]Reaction of 0.1 mmol of atroponitrile with 4 equiv. of RHgX and other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard; Yield of $RCH_2CH(Ph)CN$ in the first column; Yield of $CH_3CH(Ph)CN$ in the second column.

10. Radical Alkylations of Phenyl Vinyl Ketone[42] and α-Substituted Phenyl Vinyl Ketones

Radical *tert*-butylations of phenyl vinyl ketone give fair yield with triethylsilane and an excellent yield with phenylsilane. Since phenyl vinyl ketone is likely to polymerize, long reaction time makes alkylation unpractical. When triethylsilane is used in the *n*-butylation of phenyl vinyl ketone, it gives very good yield, whereas phenylsilane gives a low yield (Table XIX).

Table XIX. Radical Alkylations of Phenyl Vinyl Ketone[a]

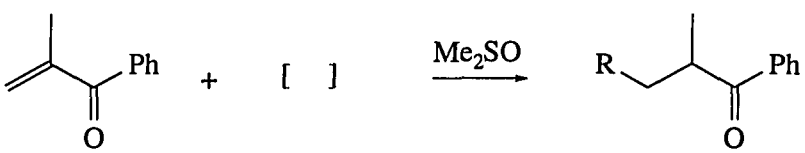


35, R = *t*-Bu
36, R = *n*-Bu

Entry	R	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)	
		RHgCl	KI	Et_3SiH	$PhSiH_3$			
1	*t*-Bu	4		4		22	66	(**35**)
2	*t*-Bu	4			4	2	91	(**35**)
3	*n*-Bu	4	2	4		3	86	(**36**)
4	*n*-Bu	4			4	2	38	(**36**)

[a]Reaction of 0.1 mmol of phenyl vinyl ketone with 4 equiv. of RHgCl and other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

Table XX. Radical Alkylations of Phenyl 2-Propenyl Ketone[a]



37, R = *t*-Bu
38, R = *n*-Bu

Entry	R	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)	
		RHgCl	KI	Et_3SiH	$PhSiH_3$			
1	*t*-Bu	4		4		12	54	(**37**)
2	*t*-Bu	4			4	1	47	(**37**)
3	*n*-Bu	4	2	4		22	40	(**38**)
4	*n*-Bu	4			4	16	7	(**38**)

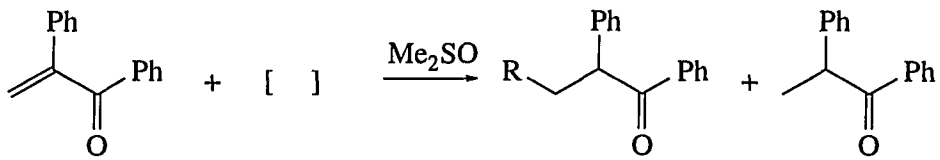
[a]Reaction of 0.1 mmol of phenyl 2-propenyl ketone with 4 equiv. of RHgCl and other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

With phenyl 2-propenyl ketone, *tert*-butylation products are obtained in fair yield with either triethylsilane or phenylsilane. Only triethylsilane gives significant yield for the *n*-butylation (Table XX).

Although radical alkylation of α-methylene deoxybenzoin[43] can be achieved with the silane system, direct reduction of the alkene by silyl hydride is also observed in all cases (Table XXI).

The more reactive alkene, 1-chlorovinyl phenyl ketone, gives a better *tert*-butylation yield with phenylsilane than triethylsilane; reduction of the alkene by phenylsilane was the major reaction observed with *n*-butylmercury chloride (Table XXII).

Table XXI. Radical Alkylations of α-Methylene Deoxybenzoin[a]

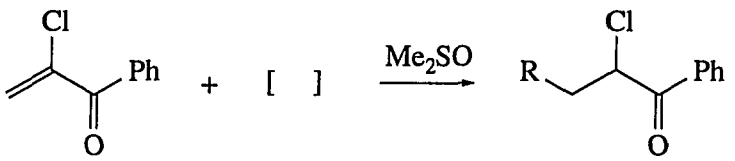


39, R = *t*-Bu
40, R = *n*-Bu

Entry	R	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)
		RHgCl	KI	Et_3SiH	$PhSiH_3$		
1	*t*-Bu	4		4		12	64 (**39**), 17
2	*t*-Bu	4			4	1	62 (**39**), 6
3	*n*-Bu	4	2	4		22	46 (**40**), 4
4	*n*-Bu	4			4	24	8 (**40**), 3

[a]Reaction of 0.1 mmol of α-methylene deoxybenzoin with other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard; Yield of $RCH_2CH(Ph)COPh$ in the first column; Yield of $CH_3CH(Ph)COPh$ in the second column.

Table XXII. Radical Alkylations of 1-Chlorovinyl Phenyl Ketone[a]



41, R = *t*-Bu
42, R = *n*-Bu

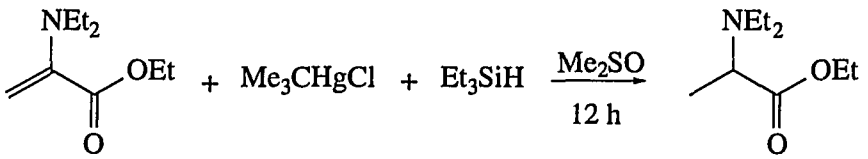
Entry	R	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)	
		RHgCl	KI	Et_3SiH	$PhSiH_3$			
1	*t*-Bu	4		4		22	43	(**41**)
2	*t*-Bu	4			4	1	69	(**41**)
3	*n*-Bu	4	4	4		22	16	(**42**)
4	*n*-Bu	4			4	3	35[c]	(**42**)

[a]Reaction of 0.1 mmol of 1-chlorovinyl phenyl ketone with other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard
[c]For BuHgCl/$PhSiH_3$ reaction, 41% of reduction product [$CH_3CH(Cl)COPh$] was observed.

11. Side Reactions in the Silane-Promoted Alkylation Reactions

Direct reductions of alkenes by silyl hydrides have been observed as a side reaction, or major reaction, for the reactions of several alkenes with alkylmercury chloride and a silane. The electrophilic catalysis by Hg(II) species of silyl hydride reduction process has been documented.[44] 1,1-Disubstituted alkenes capable of chelating with alkylmercury halide undergo primarily reduction, as is the case for ethyl α-diethylaminoacrylate (reaction 17), ethyl α-morpholinoacrylate (Table XXIII), and diethyl methylenemalonate (Table XXIV).

a. Silyl Hydride Reduction of Ethyl α-Diethylaminoacrylate[45]



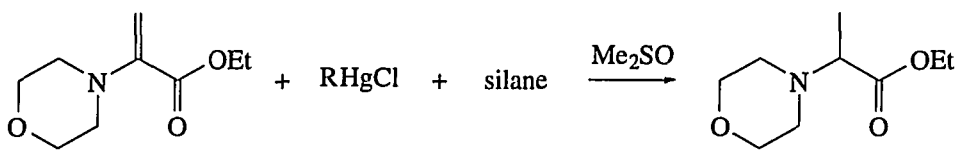
(17)

43 4 equiv. 4 equiv. **44**, 60%

b. Silyl Hydride Reduction of Ethyl α-Morpholinoacrylate[45]

The direct reduction of the substrate also occurred for mixtures of a silane and either phenylmercury chloride (entry 3 in Table XXIII) or mercury(II) chloride (entries 4 and 5).

Table XXIII. Silyl Hydride Reduction of Ethyl α-Morpholinoacrylate[a]



45 **46**

Entry	R	Silane	Time	Yield, %[b]
1	*t*-Bu	Et_3SiH	12 h	82
2	*t*-Bu	$PhSiH_3$	35 min	87
3	Ph	$PhSiH_3$	40 min	84
4	Cl	Et_3SiH	1 h	27
5	Cl	$PhSiH_3$	1 h	60

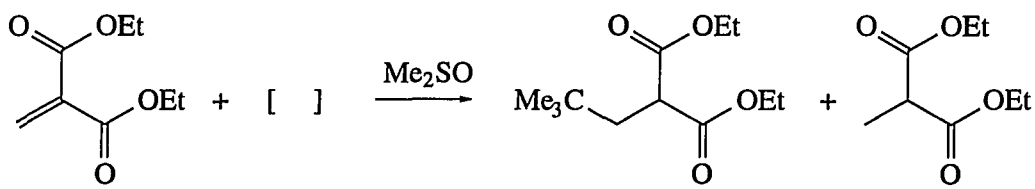
[a]Reaction of 0.1 mmol of ethyl α-morpholinoacrylate with 4 equiv. of a mercuric chloride and 4 equiv. of a silane in 4 mL of Me_2SO.

[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

c. Attempted Alkylation of Diethyl Methylenemalonate[46]

In the case of diethyl methylenemalonate, direct reduction of the substrate occurs exclusively when *n*-butylmercury chloride is used. With *tert*-butylmercury chloride a radical chain process occurs more readily and an alkylation product is also observed (Table XXIV).

Table XXIV. Radical Alkylations of Diethyl Methylenemalonate[a]



47 **48** **49**

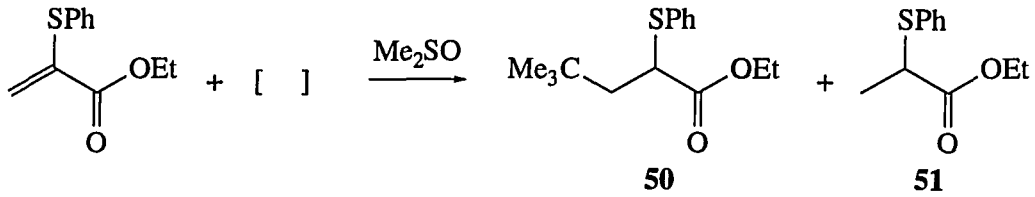
Entry	R	X	Molar Equivalent RHgX	Et$_3$SiH	PhSiH$_3$	Time (h)	Yield, %[b]
1	*t*-Bu	Cl	4	4		12	8 (**48**), 15 (**49**)
2	*t*-Bu	Cl	4		4	12	33 (**48**), 29 (**49**)
3	*n*-Bu	I	4	4		12	60 (**49**)
4	*n*-Bu	Cl	4		4	12	62 (**49**)

[a]Reaction of 0.1 mmol of diethyl methylenemalonate with other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard; Yield of $Me_3CCH_2CH(CO_2Et)_2$ in the first column; Yield of $CH_3CH(CO_2Et)_2$ in the second column.

d. Radical *tert*-Butylation of Ethyl α-Phenylthioacrylate[47]

In the case of ethyl α-phenylthioacrylate reduction is also a competing process in the alkylation with the silane system. Photostimulated alkylation with *t*-BuHgCl/KI is an available alternate reaction route although the yield is poor (Table XXV).

Table XXV. Radical *tert*-Butylations of Ethyl α-Phenylthioacrylate[a]



Entry	Molar Equivalent				Time (h)	Yield,[b] % (Prdt)	
	Me_3CHgCl	KI	Et_3SiH	$PhSiH_3$			
1	4		4		17	57 (**50**),	34 (**51**)
2	4			4	4	51 (**50**),	25 (**51**)
3	4	8			12	39 (**50**)	

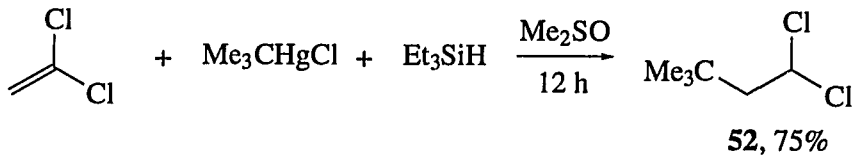
[a]Reaction of 0.1 mmol of diethyl methylenemalonate with other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard; Yield of product **50** in the first column; Yield of product **51** in the second column.

12. Radical *tert*-Butylations of Other Olefins in the Presence of A Silane

The silane system is an excellent one for reductive alkylation of electronegatively substituted alkenes. Reductive alkylation is the major reaction pathway even in cases where other reaction route is favorable in the photostimulated system. Reaction of excess of Me_3CHgCl and KI with $CH_2=C(CH_2Cl)CO_2Et$ under irradiation forms only $(Me_3CCH_2)_2CHCO_2Et$ in 80% yield via β-elimination of $Cl^•$ from the intermediate adduct radical. However, with Et_3SiH/Me_3CHgCl elimination is not as important and $Me_3CCH_2CH(CH_2Cl)CO_2Et$ is formed in 50% yield.

Following reactions were also carried out by using 4 equiv. each of Et_3SiH and Me_3CHgCl unless otherwise indicated. Yields were determined by GC and ^1H NMR integration with toluene as an added internal standard.

a. Vinylidene Chloride



(18)

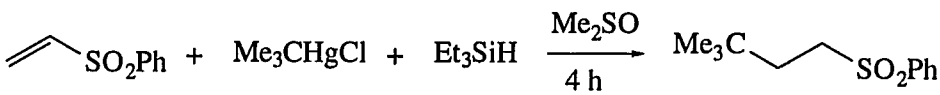
52, 75%

b. Phenyl Vinyl Sulfoxide

(19)

53, 60%

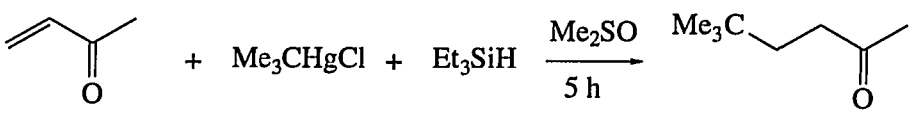
c. Phenyl Vinyl Sulfone



(20)

54, 91%

d. Methyl Vinyl Ketone



(21)

55, 69%

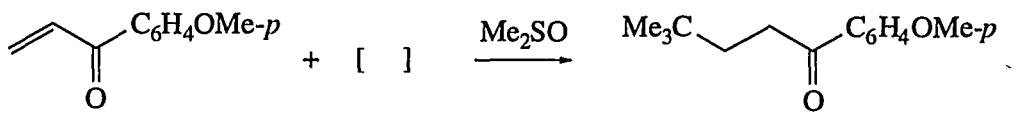
e. Diethyl Vinylphosphonate

(22)

56, 87%

f. *p*-Methoxyphenyl Vinyl Ketone[48]

Table XXVI. *tert*-Butylations of *p*-Methoxyphenyl Vinyl Ketone[a]



57 **58**

Entry	Molar Equivalent			Time (h)	Yield,[b] % (Prdt)	
	Me_3CHgCl	Et_3SiH	$PhSiH_3$			
1	4	4		12	95	(**58**)
2	4		4	2	83	(**58**)

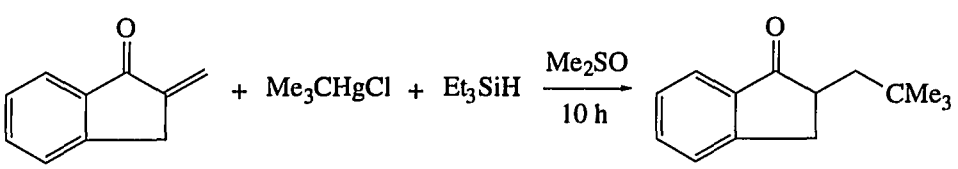
[a]Reaction of 0.1 mmol of *p*-methoxyphenyl vinyl ketone with other reagents in 4 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard

g. 1,1-Dimethylethyl Vinyl Ketone[49]

(23)

59 **60**, 78%

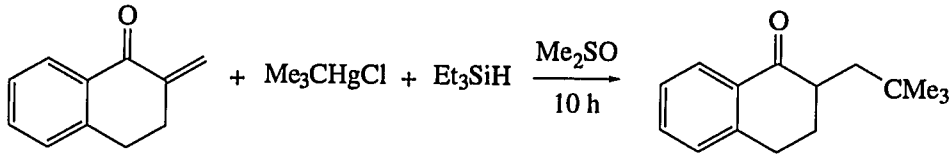
h. 2-Methylene-1-indanone[50]



(24)

61 **62**, 74%

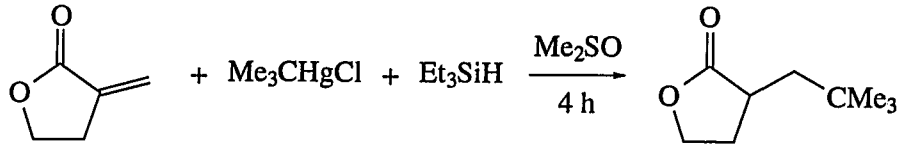
i. 2-Methylene-1-tetralone[50]



(25)

63 **64**, 90%

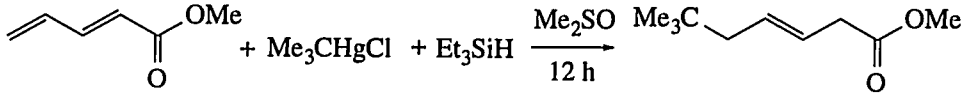
j. α-Methylene-γ-butyrolactone



(26)

65, 94%

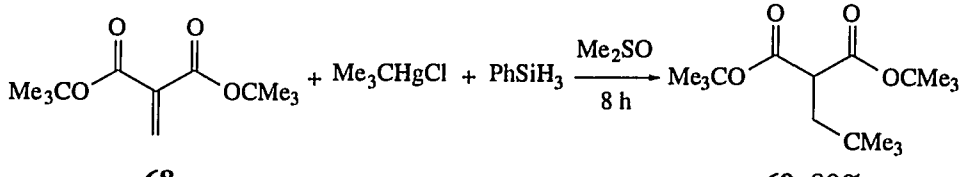
k. Methyl 2,4-Pentadienoate[51]



(27)

66 **67**, 29%

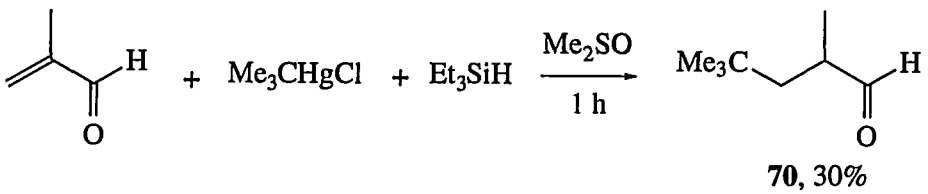
l. Bis(1,1-dimethylethyl) Methylenemalonate[46]



(28)

68 **69**, 80%

m. Methacrolein



(29)

70, 30%

D. The Effect of Silane Structure

The efficiency of the silyl hydride and alkylmercury halide combination for reductive alkylation must depend on the concentration of RHgH maintained via the reactions of Scheme VII. It seems reasonable that at equal concentrations $PhSiH_3$ would form RHgH faster than Et_3SiH and would therefore maintain a higher concentration of RHgH. With *tert*-butylmercury chloride a consistent pattern emerges. With the more reactive alkenes, e.g. $CH_2=C(Cl)CO_2Et$ or $CH_2=CHCOPh$, the two silanes give about the same yield of reductive alkylation products although the rate of reaction is much faster with $PhSiH_3$. With highly reactive alkenes, *tert*-butyl radical is efficiently trapped by the alkene and there is little competition from attack of *tert*-butyl radical upon RHgH. With less reactive alkenes, e.g. $CH_2=C(CH_3)CO_2Et$, competition between the alkene and RHgH for *tert*-butyl radical becomes important. Now, Et_3SiH which probably forms a lower steady state concentration of RHgH, gives a better yield of the reductive alkylation product than $PhSiH_3$. For *n*-butylation with *n*-butylmercury chloride yields increase from Et_3SiH to $PhSiH_3$. However, the best yields were observed from *n*-BuHgCl/KI/Et_3SiH. With KI there should be ligand exchange followed by a more rapid reaction of *tert*-butylmercury iodide with Et_3SiH. This system and $PhSiH_3$/*n*-BuHgCl are approximately equivalent with the more reactive alkenes but the *n*-BuHgCl/KI/Et_3SiH system is much better with less

reactive alkenes, e.g. $CH_2=C(CH_3)CO_2Et$, possibly *n*-butylation requires a higher steady state concentration of RHgH than *tert*-butylation for optimum yield. This could be due to a slower initiation step or an overall less efficient chain reaction. However, too rapid a formation of *n*-BuHgH such as with $PhSiH_3$ again interferes with the trapping of *n*-butyl radical by the alkene. The effects of KI were not investigated for reactions involving $PhSiH_3$ or *tert*-butylmercury chloride.

E. Conclusion

Free radical alkylation of substituted olefins promoted by the reaction of alkylmercury halides with silyl hydride compounds is a convenient method for the formation of carbon-carbon bonds. It is a particularly good procedure for the alkylation of electron-deficient alkenes. The silyl hydride method is an alternative process to the Giese borohydride method with some advantages. The silyl hydride method often does not require an excess of alkene as is usually the case with the sodium borohydride method. The reason is that in reactions where silyl hydrides are used, the low steady state concentration of alkylmercury hydride makes intermolecular alkylation more prevalent. Furthermore, the steady state concentration of the alkylmercury hydride can be controlled by the silyl hydride employed. By using the less reactive silane,[52] triethylsilane, in *tert*-butylation, a higher yield is obtained for substrates with lower reactivity. With more reactive substrates, the use of phenylsilane gives a higher yield of the *tert*-butylation product. *n*-Butylation of alkenes typically gives a higher yield with the use of triethylsilane. These observations suggest that there is a correlation between the rate of alkylmercury hydride formation and the rate of radical addition. Successful alkylation of alkenes can best be achieved by matching the reactivity of the silane with the reactivity of the substrate. Another advantage the silyl hydrides have over sodium borohydride is the

ability to tolerate a wide variety of functional groups including the aldehyde group. An important side reaction is recognized for the alkylations with the silane system. 1,1-Disubstituted alkenes capable of chelating with alkylmercury halide have the potential to be reduced by silyl hydrides.

F. Experimental Section

1. General Consideration

Analytical gas chromatography (GC) was performed on a Perkin-Elmer 3920 gas chromatograph equipped with a Hitachi D-2500 Chromato-integrator. ^{1}H and ^{13}C NMR spectra were recorded on a Nicolet NT300 spectrometer. Chemical shifts are reported in ppm from internal tetramethylsilane (300 MHz for ^{1}H NMR) or for ^{13}C NMR measured relative to the central line of internal $CDCl_3$ at 77.000 ppm (75.4 MHz for ^{13}C NMR). GCMS were recorded on a Finnegan 4000 spectrometer with Incos data system and high resolution mass spectra were recorded on a Kratos MS-50 spectrometer. Infrared spectra (IR) were recorded on an IBM IR-98 FT spectrometer or Digital FTS-7 FT spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Most products were isolated either by flash column chromatography on silica gel (Kiesel gel, 230-400 mesh ATSM, purchased from EM Regents Co.) with mixed solvents as eluents or by preparative GC. GC yields were determined by using an internal standard (toluene) and were corrected with predetermined response factors. ^{1}H NMR spectroscopy yields were determined by integration with a known amount of an internal standard (toluene).

2. Solvents and Reagents

Solvents were purchased from Fisher and Baker. Dimethyl sulfoxide (Me_2SO) was distilled from calcium hydride and stored over 4Å Molecular sieves under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium metal and benzene was distilled from calcium hydride. Other solvents were purchased and used without further purification.

Chemical reagents in high purity grades were purchased mostly from Aldrich. In most cases, the reagents were used without further purification.

3. Preparation of Organomercurials

Butylmercury chloride was prepared by a literature method,[53] while *tert*-butylmercury halides were prepared by a modified literature method. They were usually prepared from the Grignard reagents and the mercury salts (1 equiv.) in THF. Thus prepared were butylmercury chloride (lit.[54] mp 127.5 °C), *tert*-butylmercury chloride (mp found 110-113 °C, lit.[55] mp 123 °C), and *tert*-butylmercury iodide.

***tert*-Butylmercury Chloride:** *tert*-Butylmercury chloride was prepared from mercuric chloride and *tert*-butyllithium. A solution containing mercuric chloride (0.18 mol) in dry ether (500 mL) was stirred in an ice bath under nitrogen and *tert*-butyllithium (0.17 mol, 1.7 M solution in pentane) was added dropwise. After the addition, the mixture was stirred for at least 4 hours at room temperature. The mixture was then poured into water and extracted 3 times with ether (500 mL each). The combined ether layer was washed with brine solution three times and dried over anhydrous magnesium sulfate. The solution

was filtered through a celite-filled sintered glass funnel and the solvent was evaporated. The white precipitate was recrystallized from hexane-ether solution. The white needle melted at 110-113 °C; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 9H).

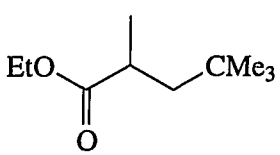
In an alternative method of preparation, a solution containing mercuric chloride (0.18 mol) in dry THF (200 mL) was stirred in an ice bath under nitrogen and *tert*-butyllithium (0.17 mol, 1.7 M solution in pentane) was added dropwise. After the addition, the mixture was stirred for 2 hours at room temperature. The solution was filtered through a celite-filled sintered glass funnel and the solvent was evaporated. The white precipitate was dissolved in 1500 mL of ether and washed three times with brine solution. Drying with anhydrous $MgSO_4$, evaporation, and two recrystallizations gave the white needles of *tert*-butylmercury chloride.

***tert*-Butylmercury Iodide:** *tert*-Butylmercury iodide was prepared by a modified anion exchange method.[56] *tert*-Butylmercury chloride (0.03 mol) was mixed with a two-fold excess of potassium iodide in 40 mL of dimethyl sulfoxide solution. The solution was stirred for 2 hours at room temperature. The reaction was quenched by adding 100 mL of water and the mixture extracted twice with ether (70 mL) and the combined organic extract filtered through a celite-filled sintered glass funnel and washed three times with water (100 mL). The solution was dried over anhydrous magnesium sulfate and the solvent was evaporated until white crystals precipitated. The solution was filtered immediately. The white crystals turned pale yellow when exposed to the air; ^{1}H NMR ($CDCl_3$) δ 1.53 (s, 9H). The material decomposed before a clear melting point could be determined.

4. Procedure for Photostimulated *tert*-Butylations of Ethyl Methacrylate

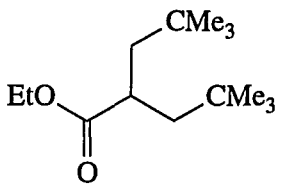
Ethyl Methacrylate (0.25 mmol), *tert*-butylmercury halide (1.0 mmol), and KI (1.0-2.0 mmol) with or without other reagents (DABCO or triethylamine) were placed in flame-dried Pyrex test tube and 5 mL of distilled and predeoxygenated dimethyl sulfoxide (Me_2SO) was added under nitrogen. With stirring the solution was irradiated with a 275 W sun lamp *ca.* 25 cm from the reaction test tube for 24 hours. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and each product was isolated by flash column chromatography (1% ethyl acetate in hexane) and characterized by instrumental analysis. Yields were determined by proton NMR integration with toluene (0.1 mmol) as an internal standard. The following products were obtained.

a. Ethyl 2,4,4-Trimethylpentanoate[57] (1)



The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.876 (s, 9H), δ 1.15 (d, 3H, *J*=7.2 Hz), δ 1.16 (dd, 1H, *J*=14.1, 3.0 Hz), δ 1.25 (t, 3H, *J*=7.2 Hz), δ 1.85 (dd, 1H, *J*=14.1, 9.3 Hz), δ 2.48 (m, 1H), δ 4.11(q, 2H, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.19, 20.45, 29.45, 30.84, 36.32, 47.81, 60.19, 178.02; GCMS *m/z* (rel intensity) 173 (M^++1, 3), 157 (16), 127 (21), 116 (67), 101 (23), 88 (39), 83 (53), 73 (38), 57 (100), 41 (67); HRMS calcd for $C_{10}H_{20}O_2$ 172.1463, found 172.1462.

b. Ethyl 4,4-Dimethyl-2-(2,2-dimethylpropyl)pentanoate (2)



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.886 (s, 18H), 1.23 (dd, 2H, *J*=14.1, 6.0 Hz), 1.255 (t, 3H, *J*=7.2 Hz), 1.73 (dd, 2H, *J*=14.1, 9.3 Hz), 2.48 (m, 1H), 4.08 (q, 2H, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0 (q), 29.5 (q), 31.2 (s), 38.4 (d), 49.3 (t), 60.1 (t), 178.5 (s); GCMS *m/z* (rel intensity) 229 (M^++1, 10), 213 (35), 157 (37), 142 (35), 129 (33), 102 (55), 83 (48), 57 (100), 41 (79).

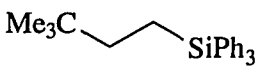
5. Procedure for *tert*-Butylation of Ethyl Methacrylate with the Silane System

Ethyl methacrylate (0.25 mmol) and *tert*-butylmercury chloride (0.5 mmol) were dissolved in a distilled and predeoxygenated Me_2SO (5 mL) in a Pyrex test tube equipped with a rubber septum. Triethylsilane (0.5 mmol) was added by syringe. The solution rapidly became cloudy from the precipitation of metallic mercury. The reaction mixture was stirred until the reaction turned clear indicating that the precipitation of metallic mercury was no longer occurring. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and proton NMR. Yields of products were measured by proton NMR integration of the product with toluene as an added internal standard.

6. Procedure for Photostimulated *tert*-Butylation of Triphenylvinylsilane

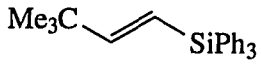
Triphenylvinylsilane (0.20 mmol), *tert*-butylmercury halide (0.6 mmol), and KI (0-2.4 mmol) with or without other reagents (DABCO or triethylamine) were placed in flame-dried Pyrex test tube and 4 mL of distilled and predeoxygenated dimethyl sulfoxide (Me_2SO) was added under nitrogen. With stirring the solution was irradiated with a 275 W sun lamp *ca.* 25 cm from the reaction test tube for 24 hours. The reaction mixture was then worked up by adding 0.22 mmol of sodium borohydride and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and each product was isolated by flash column chromatography (1% ethyl acetate in hexane) and characterized by spectra. Yields were determined by ^1H NMR integration with toluene (0.1 mmol) as an added internal standard. The following products were obtained.

a. 3,3-Dimethylbutyltriphenylsilane[24] (4)



The compound was isolated as a white solid; ^1H NMR ($CDCl_3$) δ 0.871 (s, 9H), 1.341 (m, 4H), 7.32-7.41 (m, 9H), 7.48-7.53 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 7.49, 28.80, 31.36, 37.67, 127.78, 129.28, 135.33, 135.62; GCMS *m/z* (rel intensity) 344 ($M^{+\cdot}$ 0.2), 260 (22), 259 (100), 183 (12), 181 (39), 180 (14), 155 (13), 105 (38), 57 (8), 41 (9); HRMS calcd for $C_{24}H_{28}Si$ 344.1960, found 344.1958.

b. (E)-(3,3-Dimethyl-1-butenyl)triphenylsilane[58] (5)



The compound was isolated as a solid, mp 84-86 °C. The compound was identified by ^{1}H NMR and confirmed by the comparison of the spectral data with the literature; ^{1}H NMR ($CDCl_3$) δ 1.049 (s, 9H), 6.048 (d, 1H, *J*=18.9 Hz), 6.233 (d, 1H, *J*=18.9 Hz), 7.30-7.60 (m, 15H); GCMS *m/z* (rel intensity) 342 ($M^{+\cdot}$ 13), 285 (88), 259 (77), 207 (80), 183 (89), 182 (60), 181 (98), 155 (20), 105 (100), 79 (13), 57 (12), 53 (25), 41 (20).

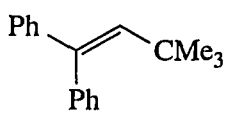
7. Procedure for *tert*-Butylation of Triphenylvinylsilane with the Silane System

Triphenylvinylsilane (0.20 mmol) and *tert*-butylmercury chloride (1.0 mmol) were dissolved in a distilled and predeoxygenated Me_2SO (5 mL) in a Pyrex test tube equipped with a rubber septum. Triethylsilane (1.0 mmol) was added by syringe. The reaction mixture was stirred until the reaction mixture turned clear after the precipitation of metallic mercury. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and proton NMR. The yield of the product was measured by proton NMR integration of the product with toluene (0.1 mmol) as an added internal standard.

8. Procedure for Photostimulated *tert*-Butylation of 1,1-Diphenylethylene

1,1-Diphenylethylene (0.20 mmol), *tert*-butylmercury iodide (0.6-2.0 mmol), $K_2S_2O_8$ (0.4 mmol), $AgNO_3$ (0.04 mmol), $CuSO_4$ (0.01 mmol), and KI (0-0.6 mmol) with or without DABCO were placed in flame-dried Pyrex test tube and 4 mL of distilled and predeoxygenated dimethyl sulfoxide was added under nitrogen. With stirring the solution was irradiated with a 275 W sun lamp *ca.* 25 cm from the reaction test tube for 24 hours. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and the product was isolated by flash column chromatography (hexane : ethyl acetate = 99 : 1) and characterized by spectra. Yields were determined by ^1H NMR integration with toluene (0.1 mmol) as an added internal standard. The following product was isolated.

a. 3,3-Dimethyl-1,1-diphenyl-1-butene[29] (7)

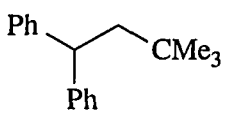


The compound was identified by ^1H NMR and confirmed by the comparison of the spectral data with the literature; ^1H NMR ($CDCl_3$) δ 0.958 (s, 9H), 6.076 (s, 1H), 7.18-7.36 (m, 10H); GCMS *m/z* (rel intensity) 236 ($M^{+\cdot}$, 62), 221 (97), 143 (100), 128 (32), 105 (33), 91 (70), 77 (13), 57 (2), 41 (14).

9. Procedure for *tert*-Butylation of 1,1-Diphenylethylene with the Silane System

1,1-Diphenylethylene (0.25 mmol) and *tert*-butylmercury chloride (2.0 mmol) were dissolved in a distilled and predeoxygenated Me_2SO (5 mL) in a Pyrex test tube equipped with a rubber septum. Triethylsilane (2.0 mmol) was added by syringe. The reaction mixture was stirred until the reaction mixture turned clear after the precipitation of metallic mercury. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with half-saturated aqueous sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and proton NMR. The yield of the product was measured by ^1H NMR integration of the product with toluene as an added internal standard. The following product was isolated.

a. 3,3-Dimethyl-1,1-diphenylbutane[59] (8)

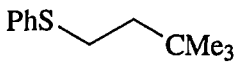


The compound was isolated as a solid, mp 32-33 °C (lit[60], mp 33 °C). The compound was identified by ^1H NMR and confirmed by the comparison of the spectral data with the literature;[59] ^1H NMR ($CDCl_3$) δ 0.827 (s, 9H), 2.09 (d, 2H, *J*=6.9 Hz), 4.048 (t, 1H, *J*=6.9 Hz), 7.20-7.33 (m, 10H).

10. Procedure for Photostimulated *tert*-Butylation of Phenyl Vinyl Sulfide

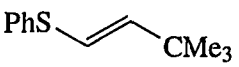
Phenyl vinyl sulfide (0.20 mmol), *tert*-butylmercury halide (0.6-1.0 mmol), $K_2S_2O_8$ (0.4 mmol), $AgNO_3$ (0.04 mmol), and $CuSO_4$ (0.01 mmol) were placed in flame-dried Pyrex test tube and 4 mL of distilled and predeoxygenated dimethyl sulfoxide was added under nitrogen. With stirring the solution was irradiated with a 275 W sun lamp *ca.* 25 cm from the reaction test tube for 20 hours. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and each product was isolated by flash column chromatography (1% ethyl acetate in hexane) and characterized by spectra. Yields were determined by ^1H NMR integration with toluene (0.1 mmol) as an added internal standard. The following products were isolated.

a. 3,3-Dimethylbutyl Phenyl Sulfide[61] (9)



The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.926 (s, 9H), 1.553 (m, 2H), 2.889 (m, 2H), 7.15-7.35 (m, 5H).

b. (E)-(3,3-Dimethyl-1-butenyl) Phenyl Sulfide[62] (10)



The compound was identified by ^1H NMR and confirmed by the comparison of the spectral data with the literature;[26] ^1H NMR ($CDCl_3$) δ 1.083 (s, 9H), 6.051 (s, 1H), 6.059 (s, 1H), 7.15-7.35 (m, 5H).

11. Procedure for *tert*-Butylation of Phenyl Vinyl Sulfide with the Silane System

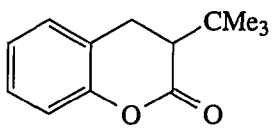
Phenyl vinyl sulfide (0.25 mmol) and *tert*-butylmercury chloride (1.0 mmol) were dissolved in a distilled and predeoxygenated Me_2SO (5 mL) in a Pyrex test tube equipped with a rubber septum. Triethylsilane (1.0-1.5 mmol) was added by syringe. The reaction mixture was stirred until the reaction mixture turned clear after the precipitation of metallic mercury. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and ^1H NMR. The yield of the product was measured by ^1H NMR integration of the product with toluene (0.1 mmol) as an added internal standard.

12. Procedure for *tert*-Butylation of Coumarin with the Silane System

Coumarin (0.25 mmol) and *tert*-butylmercury chloride (1.0 mmol) were dissolved in a distilled and predeoxygenated Me_2SO (5 mL) in a Pyrex test tube equipped with a rubber septum. Triethylsilane (0.1-1.0 mmol) was added by syringe. The reaction mixture was stirred until the reaction mixture turned clear from cloudy with precipitation of metallic mercury. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic

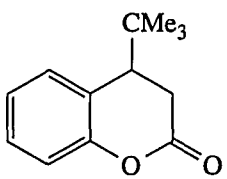
extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and proton NMR. The yield of the product was measured by ^1H NMR integration of the product with toluene (0.1 mmol) as an added internal standard. The following products were isolated.

a. 3-(1,1-Dimethylethyl)dihydrocoumarin (11)



The compound was isolated as a white solid, mp 45-46 °C; ^1H NMR ($CDCl_3$) δ 1.082 (s, 9H), 2.503 (dd, 1H, *J*=9.6, 6.6 Hz), 2.947 (dd, 1H, *J*=16.2, 9.6 Hz), 3.065 (dd, 1H, *J*=16.2, 6.6 Hz), 6.96-7.27 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 25.96 (t), 27.96 (q), 32.89 (s), 48.72 (d), 116.1 (d), 123.2 (s), 124.0 (d), 127.7 (d), 128.0 (d), 151.7 (s), 168.9 (s); GCMS *m/z* (rel intensity) 204 (M^+, 96), 189 (77), 168 (39), 148 (60), 133 (100), 120 (26), 119 (15), 107 (92), 91 (29), 83 (18), 77 (15), 57 (42), 55 (17); HRMS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1149.

b. 4-(1,1-Dimethylethyl)dihydrocoumarin[63] (12)



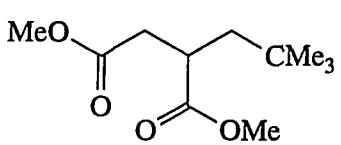
The compound was isolated as a white solid, mp 43-45 °C; ^1H NMR ($CDCl_3$) δ 0.954 (s, 9H), 2.68 (dd, 1H, *J*=7.5, 15.9 Hz), 2.75 (d, 1H, *J*=7.5 Hz), 3.05 (d, 1H, *J*=15.9 Hz), 7.04-7.31 (m, 4H); GCMS *m/z* (rel intensity) 204 (M^+, 11), 148 (100), 91

(20), 57 (85); HRMS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1151; FTIR ($CDCl_3$) 2966 (m), 2901 (w), 1765 (s) cm^{-1}.

13. Procedure for Photostimulated *tert*-Butylation of Dimethyl Itaconate

Dimethyl itaconate (0.10 mmol), *tert*-butylmercury halide (0.1-0.4 mmol), with or without other reagents were placed in flame-dried Pyrex test tube and 4 mL of distilled and predeoxygenated dimethyl sulfoxide was added under nitrogen. With stirring the solution was irradiated with a 275 W sun lamp *ca.* 25 cm from the reaction test tube for 12 hours. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and each product was isolated by flash column chromatography (hexane : ethyl acetate = 99 : 1) and characterized by spectra. Yields were determined by proton NMR integration with toluene (0.1 mmol) as an added internal standard. The following products were isolated.

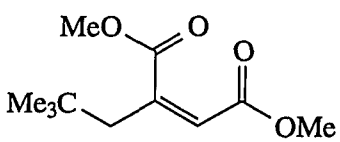
a. Dimethyl (2,2-Dimethylpropyl)succinate (14)



The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.904 (s, 9H), 1.25 (dd, 1H, *J*=14.1, 3.6 Hz), 1.76 (dd, 1H, *J*=14.1, 8.4 Hz), 2.43 (dd, 1H, *J*=16.2, 6.0 Hz), 2.64 (dd, 1H, *J*=16.2, 7.8 Hz), 2.88 (m, 1H), 3.665 (s, 3H), 3.682 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 29.26 (q), 30.79 (s), 37.99 (d), 38.48 (t), 45.77 (t), 51.70 (q), 51.82

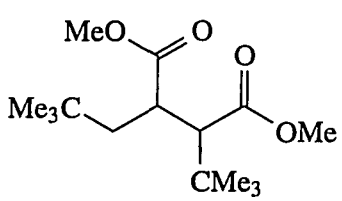
(q), 171.99 (s), 176.36 (s); GCMS *m/z* (rel intensity) 201 (M^+-15, 4), 185 (31), 169 (18), 160 (35), 143 (45), 141 (58), 128 (80), 109 (31), 100 (66), 87 (47), 57 (100), 41 (47); HRMS calcd for $C_{11}H_{20}O_4$ 216.1362, found 216.1362; FTIR (neat) 2957 (s), 1744 (vs), 1439 (w), 1250 (m), 1161 (m) cm^{-1}.

b. Dimethyl (2,2-Dimethylpropyl)maleate[64] (15)



The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.888 (s, 9H), 2.905 (s, 2H), 3.748 (s, 3H), 3.788 (s, 3H), 6.719 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 29.39 (q), 33.16 (s), 39.08 (t), 51.60 (q), 52.47 (q), 127.08 (d), 148.85 (s), 166.23 (s), 168.75 (s); GCMS *m/z* (rel intensity) 199 (M^+-15, 0.4), 183 (5), 167 (9), 158 (24), 126 (100), 98 (22), 68 (11), 57 (52), 41 (29); HRMS calcd for $C_{11}H_{18}O_4$ 214.1205, found 214.1200; FTIR (neat) 2955 (m), 1728 (vs), 1256 (m) cm^{-1}.

c. Dimethyl 2-(1,1-Dimethylethyl)-3-(2,2-dimethylpropyl)-succinate (16)



The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.877 (s, 9H), 1.018 (s, 9H), 1.40 (dd, 1H, *J*-1.8, 14.1 Hz), 2.02 (dd, 1H, *J*=4.7, 13.8 Hz), 2.30 (d, 1H, *J*=3.9 Hz), 2.82 (ddd, 1H, *J*=1.8, 3.9, 11.4 Hz), 3.619 (s, 3H), 3.629 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 27.870 (q), 29.284 (q), 31.145 (s), 34.185 (s), 41.202 (d), 48.814 (t),

51.126 (q), 51.555 (q), 60.779 (d), 173.510 (s), 176.043 (s); GCMS *m/z* (rel intensity) 257 (M^+-15, 1), 241 (8), 225 (7), 216 (10), 184 (11), 169 (17), 159 (57), 83 (40), 57 (100), 41 (53); FTIR (neat) 2957 (m), 2872 (w), 1744 (s) cm^{-1}.

14. Procedure for *tert*-Butylation of Dimethyl Itaconate with the Silane System

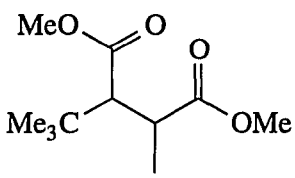
Dimethyl itaconate (0.10 mmol) and *tert*-butylmercury chloride (0.4 mmol) were dissolved in a distilled and predeoxygenated Me_2SO (4 mL) in a Pyrex test tube equipped with a rubber septum. Triethylsilane (0.4 mmol) was added by syringe. The reaction mixture was stirred until the reaction mixture turned clear after precipitation of metallic mercury. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and ^1H NMR. The yield of the product was measured by ^1H NMR integration of the product with toluene (0.1 mmol) as an added internal standard.

15. Procedure for Photostimulated *tert*-Butylation of Dimethyl Citraconate

Dimethyl citraconate (0.10 mmol), *tert*-butylmercury halide (0.1-0.4 mmol), with or without other reagents were placed in flame-dried Pyrex test tube and 4 mL of distilled and predeoxygenated dimethyl sulfoxide was added under nitrogen. With stirring the solution was irradiated with a 275 W sun lamp *ca.* 25 cm from the reaction test tube for 12 hours. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic

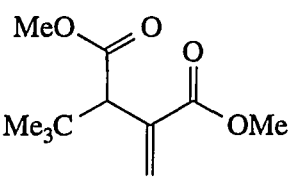
extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and each product was isolated by flash column chromatography (1% ethyl acetate in hexane) and characterized by instrumental analysis. Yields were determined by ^1H NMR integration with toluene (0.1 mmol) as an added internal standard. The following products were isolated.

a. Dimethyl 2-(1,1-Dimethylethyl)-3-methylsuccinate (19)



The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 1.028 (s, 9H), 1.322 (d, 3H, *J*=7.2 Hz), 2.422 (d, 3H, *J*=7.2 Hz), 2.907 (dq, 3H, *J*=7.2, 7.2 Hz), 3.635 (s, 3H), 3.643 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 19.15 (q), 28.50 (q), 33.26 (s), 39.70 (d), 51.02 (q), 51.70 (q), 58.46 (d), 174.3 (s), 176.2 (s); GCMS *m/z* (rel intensity) 185 (M^+-31, 11), 169 (9), 160 (40), 128 (100), 101 (43), 69 (36), 57 (50), 41 (30); HRMS calcd for $C_{11}H_{20}O_4$ 216.1362, found 216.1358.

b. Dimethyl 2-(1,1-Dimethylethyl)-3-methylenesuccinate (20)



The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 1.028 (s, 9H), 1.322 (d, 3H, *J*=7.2 Hz), 2.422 (d, 3H, *J*=7.2 Hz), 2.907 (dq, 3H, *J*=7.2, 7.2 Hz), 3.635 (s,

3H), 3.643 (s, 3H); GCMS *m/z* (rel intensity) 199 (M^+-15, 2), 183 (4), 167 (7), 158 (21), 139 (5), 126 (100), 98 (18), 57 (46), 41 (19).

16. Preparations of Commercially Unavailable Alkenes

Preparations of Dimethyl Itaconate (13) and Dimethyl Citraconate (18): Itaconic acid or citraconic acid (25 mmol) was dissolved in 40 mL of methanol. With stirring a catalytic amount of concentrated H_2SO_4 (2 mL) was added slowly. The reaction mixture was refluxed (*ca.* 90 °C) for 2 hours and cooled to room temperature, and then poured into 50 mL of water. The mixture was extracted three times with CH_2Cl_2 (30 mL). The methylene chloride solution was washed with water (100 mL), 5% $NaHCO_3$ solution (100 mL) and water (100 mL), and then dried over anhydrous $MgSO_4$. After filtration, the methylene chloride was evaporated under vacuum. Vacuum distillation gave dimethyl itaconate (77-79 °C / 0.6 mmHg, 2.83 g, 72% yield) and dimethyl citraconate (68-71 °C / 1.0 mmHg, 3.45 g, 87% yield). ^1H NMR ($CDCl_3$) δ 3.345 (s, 2H), 3.700 (s, 3H), 3.769 (s, 3H), 5.718 (d, 1H, *J*=0.6 Hz), 6.332 (s, 1H) for dimethyl itaconate, δ 2.06 (d, 3H, *J*=1.5 Hz), 3.719 (s, 3H), 3.825 (s, 3H), 5.85 (q, 1H, *J*=1.5 Hz) for dimethyl citraconate.

Preparation of Ethyl 2-Phenylacrylate: Ethyl phenylacetate (25 mmol) and paraformaldehyde (50 mmol) were dissolved in 50 mL of absolute ethanol. A catalytic amount of NaOH (0.5 g) was added to the reaction solution. The reaction mixture was heated to reflux for 4 hours and cooled to room temperature, and then poured to 50 mL of water. The aqueous solution was extracted three times with ether (30 mL). The ether extract was then washed with water (50 mL), 10% HCl solution (50 mL), 5% $NaHCO_3$

solution (50 mL), and then dried over anhydrous $MgSO_4$. The ether was evaporated under vacuum. Ethyl 2-phenylacrylate was purified by flash column chromatography (5% of ethyl acetate in hexane). ^1H NMR ($CDCl_3$) δ 1.330 (t, 3H, *J*=7.2 Hz), 4.29 (q, 2H, *J*=7.2 Hz), 5.882 (d, 1H, *J*= 1.2 Hz), 6.343 (d, 1H, *J*=1.2 Hz), 7.30-7.44 (m, 5H).

Preparation of Ethyl α,β-Dichloropropionate:[40] Ethyl acrylate (0.1 mol) was chlorinated by bubbling chlorine into a mixture of ethyl acrylate (0.1 mol) and DMF (3.0 mmol) After absorption of theoretical quantity of chlorine, the reaction mixture was stirred at room temperature for 4 hours. Ethyl α,β-dichloropropionate was collected by vacuum distillation (67-70 °C / 14 mmHg, 80% yield). ^1H NMR δ 1.334 (t, 3H, *J*=7.2 Hz), 3.807 (dd, 1H, *J*=5.4, 11.1 Hz), 3.974 (dd, 1H, *J*=8.7, 11.1 Hz), 4.300 (q, 2H, *J*=7.2 Hz), 4.421 (dd, 1H, *J*=5.4, 8.7 Hz).

Preparation of Ethyl 2-Chloroacrylate:[65] A mixture of ethyl α,β-dichloro-propionate (0.7 mmol) and quinoline (0.1 mol) was heated to 100 °C under nitrogen atmosphere for 10 min. and cooled to room temperature, and then poured to 50 mL of water. The resulting mixture was extracted three times with methylene chloride (30 mL). The combined methylene chloride extract was washed with water (50 mL), 10% HCl solution (50 mL), 5% $NaHCO_3$ solution (50 mL), and then dried over anhydrous $MgSO_4$. Methylene chloride was evaporated under vacuum. Ethyl 2-chloroacrylate was collected by vacuum distillation (51-53 °C / 18 mmHg, 62% yield). ^1H NMR δ 1.346 (t, 3H, *J*=7.2 Hz), 4.296 (q, 2H, *J*=7.2 Hz), 6.002 (d, 1H, *J*=1.5 Hz), 6.521 (d, 1H, *J*=1.2 Hz).

Preparation of Atroponitrile:[41] A solution of 0.7 g (30 mmol) of sodium dissolved in 50 mL of methanol was prepared in a 250-mL flask. To this solution was added with stirring 22 g (0.733 mol) of paraformaldehyde at a temperature of 50-55 °C.

After a solution was formed, 78 g (0.666 mol) of phenylacetonitrile was added dropwise during 20 min, After the exothermic reaction was over, stirring was continued for 90 min. at 55-60 °C. The mixture was then neutralized by adding the required amount of a dry HCl-methanol solution and concentrated under vacuum. Atroponitrile was collected by vacuum distillation (200 °C / 2.5 mmHg, 70% yield). ^{1}H NMR ($CDCl_3$) δ 6.084 (s, 1H), 6.314 (s, 1H), 7.36-7.43 (m, 3H), 7.55-7.61 (m, 2H).

Preparation of Phenyl Vinyl Ketone: Phenyl vinyl ketone was prepared by the Grignard reaction of benzaldehyde and vinylmagnesium bromide in THF solution[66] followed by Jones oxidation.[67] Phenyl vinyl ketone was purified by flash column chromatography (hexane : ethyl acetate = 20 : 1). The compound was identified by ^{1}H NMR and confirmed by comparison of spectral data with the literature;[42] ^{1}H NMR ($CDCl_3$) δ 5.92 (dd, 1H, *J*=1.5, 13.5 Hz), 6.43 (dd, 1H, *J*=1.5, 17.1 Hz), 7.15 (dd, 1H, *J*=13.5, 17.1 Hz), 7.42-7.59 (m, 3H), 7.90-7.96 (m, 2H).

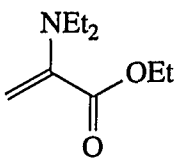
Preparation of Phenyl 2-Propenyl Ketone: Phenyl 2-propenyl ketone was prepared by bromination of isobutyrophenone with NBS in CCl_4 followed by elimination of hydrogen bromide with DBU in benzene.[68] ^{1}H NMR ($CDCl_3$) δ 2.075 (s, 3H), 5.623 (s, 1H), 5.913 (s, 1H), 7.38-7.46 (m, 2H), 7.48-7.56 (m, 1H), 7.68-7.75 (m, 2H).

Preparation of α-Methylene Deoxybenzoin or 1-Chlorovinyl Phenyl Ketone: α-Methylene deoxybenzoin or 1-chlorovinyl phenyl ketone was prepared by condensation reaction of deoxybenzoin or chloromethyl phenyl ketone with formaldehyde in methanol.[69] Products were identified by ^{1}H NMR and confirmed by comparison of spectral data with the literature; ^{1}H NMR ($CDCl_3$) δ 5.639 (s, 1H), 6.065 (s, 1H), 7.29-

7.37 (m, 3H), 7.38-7.57 (m, 5H), 7.87-7.92 (m, 2H) for α-methylene deoxybenzoin; δ 6.094 (d, 1H, *J*=2.1 Hz), 6.293 (d, 1H, *J*=1.8 Hz), 7.44-7.51 (m, 2H), 7.56-7.63 (m, 1H), 7.77-7.82 (m, 2H) for 1-chlorovinyl phenyl ketone.

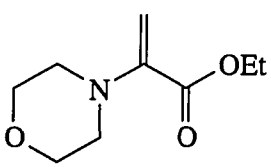
Preparation of Ethyl 2-Diethylaminoacrylate (43) and Ethyl 2-(4-Morpholino)acrylate (45): Compounds **43** and **45** were prepared by addition of diethylamine or morpholine to ethyl 2-chloroacrylate followed by elimination of hydrogen chloride.[45] Following compounds were identified by ^{1}H NMR and were used in reactions immediately after vacuum distillation.

a. Ethyl 2-Diethylaminoacrylate (43)



The compound was purified as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.067 (t, 6H, *J*=7.2 Hz), 1.321 (t, 3H, *J*=7.2 Hz), 3.023 (q, 4H, *J*=7.2 Hz), 4.249 (q, 2H, *J*=7.2 Hz), 4.324 (s, 1H), 4.902 (s, 1H).

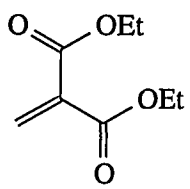
b. Ethyl 2-(4-Morpholino)acrylate (45)



The compound was purified as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.327 (t, 3H, *J*=7.2 Hz), 2.886 (t, 4H, *J*=4.8 Hz), 3.803 (t, 4H, *J*=7.2 Hz), 4.614 (s, 1H), 5.256 (s, 1H).

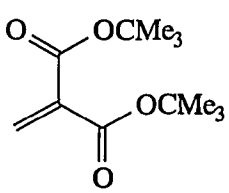
Preparation of Diethyl Mehtylenemalonate (47) and Bis(1,1-dimethyl-ethyl) Methylenemalonate (68): Compounds **47** and **68** were prepared by the literature method.[46] Following compounds were identified by ^{1}H NMR and confirmed by comparison of spectral data with literature.[70]

a. Diethyl Methylenemalonate (47)



The compound was purified by vacuum distillation; ^{1}H NMR ($CDCl_3$) δ 1.328 (t, 6H, *J*=7.2 Hz), 4.286 (q, 4H, *J*=7.2 Hz), 6.509 (s, 2H).

b. Bis(1,1-dimethylethyl) Methylenemalonate (68)



The compound was purified by vacuum distillation; ^{1}H NMR ($CDCl_3$) δ 1.512 (s, 18H), 6.246 (s, 2H).

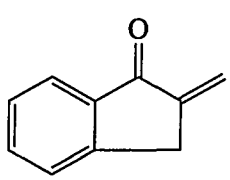
Preparation of Ethyl α-Phenylthioacrylate: Ethyl α-phenylthioacrylate was prepared by the literature method.[47] The compound was identified by ^{1}H NMR and confirmed by the comparison of the spectral data with the literature; ^{1}H NMR ($CDCl_3$) δ 1.282 (t, 3H, *J*=7.2 Hz), 4.255 (q, 2H, *J*=7.2 Hz), 5.247 (s, 1H), 6.321 (s, 1H), 7.33-7.42 (m, 3H), 7.44-7.50 (m, 2H).

Preparation of *p*-Methoxyphenyl Vinyl Ketone (57): *p*-Methoxyphenyl vinyl ketone was prepared by the literature method.[48] The compound was identified by ^{1}H NMR and confirmed by comparison of spectral data with the literature; ^{1}H NMR ($CDCl_3$) δ 3.876 (s, 3H), 5.871 (dd, 1H, *J*=1.5, 10.5 Hz), 6.424 (dd, 1H, *J*=1.5, 17.1 Hz), 6.92-6.99 (m, 2H), 7.175 (dd, 1H, *J*=10.5, 17.1 Hz), 7.92-7.99 (m, 2H).

Preparation of 1,1-Dimethylethyl Vinyl Ketone (59): 1,1-Dimethylethyl vinyl ketone was prepared by literature method.[50] The compound was identified by ^{1}H NMR and confirmed by comparison of spectral data with the literature;[71] ^{1}H NMR ($CDCl_3$) δ 1.181 (s, 9H), 5.703 (dd, 1H, *J*=1.8, 10.5 Hz), 6.362 (dd, 1H, *J*=1.8, 17.1 Hz), 6.836 (dd, 1H, *J*=10.5, 17.1 Hz).

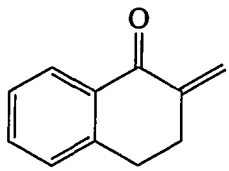
Preparation of 2-Methylene-1-indanone (61) and 2-Methylene-1-tetralone (63): Compounds **61** and **63** were prepared by the literature method.[50] Following compounds were identified by ^{1}H NMR.

a. 2-Methylene-1-indanone (61)



The compound was purified as a liquid; ^{1}H NMR ($CDCl_3$) δ 3.757 (s, 2H), 5.643 (s, 1H), 6.367 (s, 1H), 7.404 (s, 1H), 7.493 (d, 1H, *J*=7.5 Hz), 7.606 (m, 1H), 7.865 (d, 1H, *J*=7.8 Hz).

b. 2-Methylene-1-tetralone (63)



The compound was purified as a liquid; ^{1}H NMR ($CDCl_3$) δ 2.862 (m, 2H), 3.005 (m, 2H), 5.451 (s, 1H), 6.228 (s, 1H), 7.239 (d, 1H, *J*=6.6 Hz), 7.343 (m, 1H), 7.482 (m, 1H), 8.113 (d, 1H, *J*=7.5).

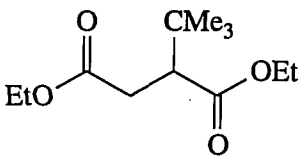
Preparation of Methyl 2,4-Pentadienoate (66): Methyl 2,4-pentadienoate was prepared by the literature method.[51] The compound was purified by vacuum distillation and identified by ^{1}H NMR; ^{1}H NMR ($CDCl_3$) δ 3.754 (s, 3H), 5.495 (d, 1H, *J*=9.6 Hz), 5.611 (d, 1H, *J*=17.1 Hz), 5.916 (d, 1H, *J*=15.6 Hz), 6.458 (m, 1H), 7.275 (dd, 1H, *J*=10.8, 15.6 Hz).

17 General Procedure for Alkylation of Alkenes with the Silane System

The substrate (0.10 mmol) and alkylmercury halide (0.4 mmol of either *tert*-butylmercury chloride or *n*-butylmercury halide) with or without KI (0.2-0.4 mmol) were dissolved in a distilled and predeoxygenated Me_2SO (4 mL) in a Pyrex test tube equipped with a rubber septum. A silyl hydride (0.4 mmol of either triethylsilane or phenylsilane) was added by syringe. The reaction mixture was stirred until the reaction mixture turned clear after the precipitation of metallic mercury. The reaction mixture was then poured into 15 mL of saturated sodium thiosulfate solution and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with half-saturated sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under

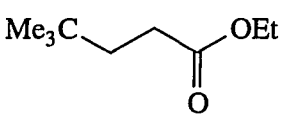
vacuum. The mixture was analyzed by GC and proton NMR. The yield of the product was measured by proton NMR integration of the product with toluene (0.1 mmol) as an added internal standard. The following products were isolated.

a. Diethyl (1,1-Dimethylethyl)succinate[72]



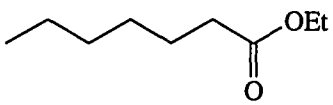
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9H), 1.24 (t, 3H, *J*=7.2 Hz), 1.27 (t, 3H, *J*=7.2 Hz), 2.78 (dd, 1H, *J*=12.0, 16.2 Hz), 4.07-4.21 (m, 4H); GCMS *m/z* (rel intensity) 231 (M^++1, 0.2), 215 (0.4), 185 (42), 174 (43), 128 (100), 110 (14), 100 (26), 83 (16), 69 (15), 57 (31); HRMS calcd for $C_{12}H_{22}O_4$ 230.1518, found 230.1515; FTIR (neat) 2968 (m), 2907 (w), 1728 (s), 1161 (s) cm^{-1}.

b. Ethyl 4,4-Dimethylpentanoate[73] **(21)**



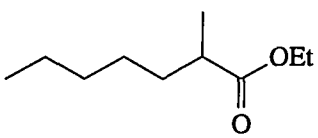
The compound was identified by ^{1}H NMR and GCMS after isolation and confirmed by comparison with the literature;[55,74] ^{1}H NMR ($CDCl_3$) δ 0.896 (s, 9H), 1.25 (t, 3H, *J*=7.2 Hz), 1.55 (t, 2H, *J*=8.4 Hz), 2.27 (t, 2H, *J*=8.4 Hz), 4.12 (q, 2H, *J*=7.2 Hz); GCMS *m/z* (rel intensity) 158 (M^+, 0.1), 143 (12), 114 (29), 101 (100), 71 (80), 57 (88), 41 (90).

c. Ethyl Heptanoate (22)



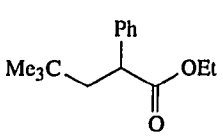
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.883 (t, 3H, *J*=6.9 Hz), 1.253 (t, 3H, *J*=7.2 Hz), 1.289 (m, 6H), 1.616 (m, 2H), 2.286 (t, 3H, *J*=7.2 Hz), 4.122 (q, 2H, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.04 (q), 14.23 (q), 22.48 (t), 24.94 (t), 28.79 (t), 31.45 (t), 34.39 (t), 60.11 (t), 173.9 (s); GCMS *m/z* (rel intensity) 158 (M^+, 2), 113 (30), 101 (23), 88 (100), 73 (22), 70 (26), 60 (39), 55 (22), 43 (71), 41 (38); HRMS calcd for $C_9H_{18}O_2$ 158.1307, found 158.1310.

d. Ethyl 2-Methylheptanoate[75] (23)



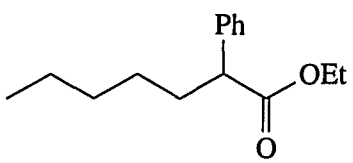
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.879 (t, 3H, *J*=6.0 Hz), 1.13 (d, 3H, *J*=6.9 Hz), 1.254 (d, 3H, *J*=6.9 Hz), 1.24-1.35 (m, 8H), 2.40 (m, 1H), 4.12 (q, 2H, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.04 (q), 14.27 (q), 17.08 (q), 22.52 (t), 26.88 (t), 31.70 (t), 33.78 (t), 39.57 (d), 60.05 (t), 176.94 (s); GCMS *m/z* (rel intensity) 172 (M^+, 1), 127 (11), 115 (15), 102 (100), 87 (11), 74 (47), 57 (64), 55 (20), 43 (30), 41 (43).

e. Ethyl 4,4-Dimethyl-2-phenylpentanoate (24)



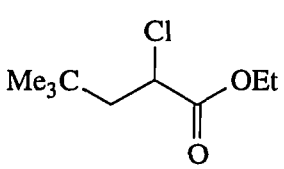
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.901 (s, 9H), 1.198 (t, 3H, *J*=7.2 Hz), 1.559 (dd, 1H, *J*=3.6, 13.8 Hz), 2.310 (dd, 1H, *J*=9.3, 14.1 Hz), 3.631 (dd, 1H, *J*=3.6, 9.3 Hz), 3.97-4.19 (m, 2H), 7.18-7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.04 (q), 29.41 (q), 31.03 (s), 47.40 (t), 48.27 (d), 60.69 (t), 126.9 (d), 127.7 (d), 128.5 (d),141.1 (s), 174.7 (s); GCMS *m/z* (rel intensity) 234 (M^+, 5), 177 (21), 161 (8), 145 (8), 105 (28), 91 (16), 77 (4), 57 (100), 41 (13); HRMS calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1616; FTIR (neat) 1736 (vs), 1150 (s) cm^{-1}.

f. Ethyl 2-Phenylheptanoate (25)



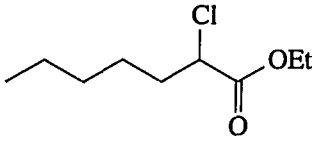
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.857 (t, 3H, *J*=6.6 Hz), 1.204 (t, 3H, *J*=7.2 Hz), 1.23-1.33 (m, 6H), 1.67-1.81 (m, 1H), 1.97-2.12 (m, 1H), 3.511 (t, 1H, *J*=7.5 Hz), 4.01-4.20 (m, 2H), 7.20-7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.01 (q), 14.14 (q), 22.42 (t), 27.24 (t), 31.54 (t), 33.58 (t), 51.80 (d), 60.56 (t), 127.0 (d), 127.9 (d), 128.4 (d), 139.4 (s), 174.1 (s); GCMS *m/z* (rel intensity) 235 (M^++1, 5), 234 (2), 164 (57), 105 (16), 91 (100), 41 (10); HRMS calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1619; FTIR (neat) 1734 (vs), 1161 (s) cm^{-1}.

g. Ethyl 2-Chloro-4,4-dimethylpentanoate (26)



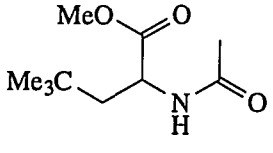
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.956 (s, 9H), 1.309 (t, 3H, *J*=7.2 Hz), 1.826 (dd, 1H, *J*=5.4, 14.7 Hz), 2.174 (dd, 1H, *J*=8.1, 14.4 Hz), 4.226 (q, 2H, *J*=7.2 Hz), 4.280 (dd, 1H, *J*=5.4, 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 13.94 (q), 29.41 (q), 30.90 (s), 48.37 (t), 54.19 (d), 61.89 (d), 170.47 (s); GCMS *m/z* (rel intensity) 193 (M^++1, 0.4), 177 (2), 141 (15), 136 (10), 113 (13), 101 (38), 57 (100), 41 (36); HRMS calcd for $C_9H_{17}ClO_2$ 192.0917, found 192.0918.

h. Ethyl 2-Chloroheptanoate (27)



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.895 (t, 2H, *J*=6.6 Hz), 1.306 (t, 3H, *J*=7.2 Hz), 1.30-1.54 (m, 6H), 1.84-2.08 (m, 2H), 4.236 (q, 2H, *J*=7.2 Hz), 4.25 (dd, 1H, *J*=5.7, 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.91 (q), 14.01 (q), 22.35 (t), 25.62 (t), 30.99 (t), 34.84 (t), 57.46 (d), 61.89 (t), 169.76 (s); GCMS *m/z* (rel intensity) 193 (M^++1, 3), 157 (5), 147 (2), 129 (7), 124 (22), 122 (80), 94 (28), 83 (42), 56 (20), 55 (100), 43 (55), 41 (66), 39 (23); HRMS calcd for $C_9H_{17}ClO_2$ 192.0917, found 192.0917.

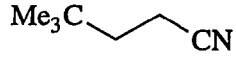
i. Methyl 2-Acetamidyl-4,4-dimethylpentanoate (28)



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.962 (s, 9H), 1.479 (dd, 1H, *J*=8.7, 14.4 Hz), 1.758 (dd, 1H, *J*=3.9, 14.4 Hz), 2.004 (s, 3H), 3.720 (s,

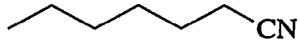
3H), 4.657 (ddd, 1H, *J*=3.9, 8.7, 8.7 Hz), 6.004 (d, 1H, *J*=7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 23.16 (q), 29.47 (q), 30.67 (s), 46.07 (t), 49.79 (d), 52.25 (q), 169.53 (s), 174.03 (s); GCMS *m/z* (rel intensity) 201 (M^+, 1), 186 (2), 156 (17), 142 (49), 102 (70), 86 (49), 57 (51), 44 (100), 43 (93), 42 (40), 41 (38); HRMS calcd for $C_{10}H_{19}O_3N$ 201.1365, found 201.1365; FTIR (neat) 3288 (b), 3076 (w), 2957 (m), 1751 (vs), 1657 (s) cm^{-1}.

j. 4,4-Dimethylpentanenitrile (29)



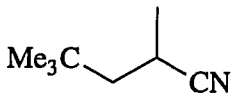
The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.929 (s, 9H), 1.615 (t, 2H, *J*=8.4 Hz), 2 282 (t, 2H, *J*=8 4 Hz); ^{13}C NMR ($CDCl_3$) δ 12.75, 28.66, 30.35, 39.21, 127.80; GCMS *m/z* (rel intensity) 111 (M^+, 1), 97 (5), 96 (100), 95 (8), 83 (2), 79 (8), 71 (6), 69 (29); HRMS calcd for $C_6H_{10}N$ (M^+-CH_3) 96.0813, found 96.0812.

k. Heptanenitrile[76] (30)



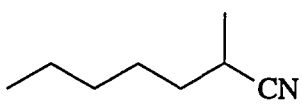
The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.903 (t, 3H, *J*=6.9 1H), 1.32 (m, 4H), 1.45 (m, 2H), 1.658 (m, 2H), 2.336 (t, 2H, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 13.8 (q), 17.1 (t), 22.3 (t), 25.3 (t), 28.3 (t), 30.9 (t), 119.8 (s); GCMS *m/z* (rel intensity) 112 (M^++1, 2), 110 (3), 96 (7), 83 (38), 82 (75), 68 (14), 55 (31), 54 (42), 43 (100), 39 (33); FTIR (neat) 2959 (s), 2934 (s), 2247 (m), 1468 (w) cm^{-1}.

l. 2,4,4-Trimethylpentanenitrile[77] (31)



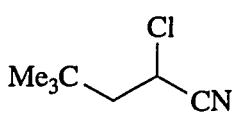
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.997 (s, 9H), 1.315 (dd, 1H, *J*=14.1, 3.0 Hz), 1.337 (d, 3H, *J*=7.2 Hz), 1.733 (dd, 1H, *J*=14.1, 10.2 Hz), 2.592 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 20.51 (q), 21.11 (d), 29.31 (q), 30.80 (s), 48.32 (t), 124.24 (s); GCMS *m/z* (rel intensity) 110 (M^+-15, 39), 83 (10), 69 (35), 68 (13), 57 (100), 55 (41); FTIR (neat) 2965 (s), 1473 (w), 1246 (w) cm^{-1}.

m. 2-Methylheptanenitrile[78] (32)



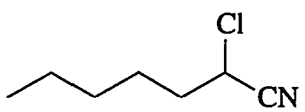
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.902 (t, 3H, *J*=6 9 Hz), 1.31 (d, 3H, *J*=7.2 Hz), 1.32 (m, 2H), 1.40-1.68 (m, 6H), 2.60 (tq, 1H, *J*=5.4, 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 13 98 (q), 18 05 (q), 22 42 (t), 25 53 (d), 26 72 (t), 31.22 (t), 34.00 (t), 123 10 (s); GCMS *m/z* (rel intensity) 126 (M^++1, 4), 124 (4), 110 (10), 97 (62), 96 (56), 82 (34), 68 (39), 55 (84), 43 (100), 41 (81); HRMS calcd for $C_6H_{10}N$ (M^+-C_2H_5) 96.0813, found 96.0812.

n. 2-Chloro-4,4-dimethylpentanenitrile[79] (33)



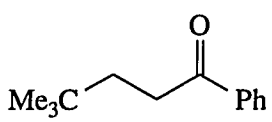
The compound was isolated as a liquid and identified by comparison of its spectral data with the literature; ^{1}H NMR ($CDCl_3$) δ 1.046 (s, 9H), 1.976 (dd, 1H, *J*=5.4, 14.4 Hz), 2.174 (dd, 1H, *J*=9.0, 14.4 Hz), 4.436 (dd, 1H, *J*=5.4, 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 29.28, 31.19, 39.31, 50.24, 118.15.

o. 2-Chloroheptanenitrile (34)



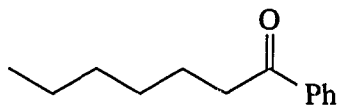
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.916 (t, 3H, *J*=6.9 Hz), 1.35 (m, 4H), 1.57 (m, 2H), 2.05 (m, 2H), 4.439 (t, 1H, *J*=6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 13.8 (q), 22.3 (t), 25.3 (t), 30.6 (t), 36.2 (t), 42.5 (d), 117.1 (s); GCMS *m/z* (rel intensity) 146 (M^++1, 2), 130 (2), 116 (11), 110 (5), 82 (48), 68 (51), 43 (100), 41 (91), 39 (38); HRMS calcd for C_6H_9ClN (M^+-CH_3) 130.0424, found 130.0426.

p. 4,4-Dimethyl-1-phenyl-1-pentanone[56] (35)



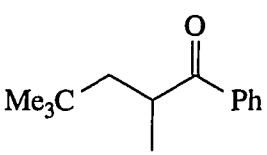
The compound was identified by ^{1}H NMR and GCMS after isolation and confirmed by comparison with the literature;[80] ^{1}H NMR ($CDCl_3$) δ 0.945 (s, 9H), 1.644 (t, 2H, *J*=8.1 Hz), 2.935 (t, 2H, *J*=8.4 Hz) 7.41-7.56 (m, 3H), 7.92-7.98 (m, 2H); GCMS *m/z* (rel intensity) 190 (M^+, 6), 175 (5), 133 (21), 105 (100), 77 (31), 57 (7).

q. 1-Phenyl-1-heptanone[81] (36)



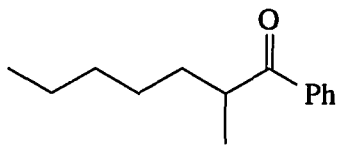
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.892 (t, 3H, *J*=6.9 Hz), 1.336 (m, 6H), 1.734 (m, 2H), 2.962 (t, 2H, *J*=7.5 Hz), 7.45 (m, 2H), 7.55 (m, 1H), 7.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.5 (t), 24.3 (t), 29.1 (t), 31.7 (t), 38.6 (t), 128.0 (d), 128.5 (d), 132.8 (d), 137.0 (s), 200.5 (s); GCMS *m/z* (rel intensity) 190 (M^+, 9), 133 (8), 120 (81), 105 (100), 77 (42), 51 (12), 41 (8); HRMS calcd for $C_{13}H_{18}O$ 190.1358, found 190.1362; FTIR (neat) 2955 (m), 2930 (s), 1688 (vs), 1448 (m) cm^{-1}.

r. 1-Phenyl-2,4,4-trimethyl-1-pentanone (37)



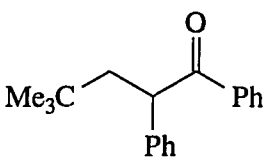
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.856 (s, 9H), 1.185 (d, 3H, *J*=7.2 Hz), 1.238 (dd, 1H, *J*=3.0, 14.1 Hz), 2.203 (dd, 1H, *J*=8.7, 14.1 Hz), 3.588 (ddd, 1H, *J*=3.0, 7.2, 8.7 Hz) 7.42-7.50 (m, 2H), 7.52-7.59 (m, 1H), 7.95-8.01 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.87 (q), 29.86 (q), 30.90 (s), 36.75 (d), 46.88 (t) 128.2 (d), 128.6 (d), 132.745 (d), 132.7 (d), 136.6 (s), 204.6 (s); GCMS *m/z* (rel intensity) 204 (M^+, 2), 189 (4), 147 (22), 105 (100), 77 (45), 57 (21), 41 (22); HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1509; FTIR (neat) 2932 (s), 1686 (vs) cm^{-1}.

s. 2-Methyl-1-phenyl-1-heptanone (38)



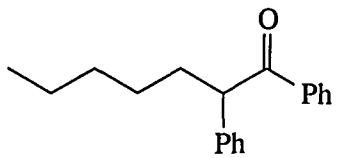
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.858 (t, 3H *J*=6.6 Hz), 1.190 (d, 3H, *J*=6.9 Hz), 1.22-1.50 (m, 7H), 1.790 (m, 1H), 3.462 (m, 1H) 7.46 (m, 2H), 7.55 (m, 1H), 7.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04 (q), 17.24 (q), 22.52 (t), 27.08 (t), 31.93 (t), 33.68 (t), 40.57 (d) 128.18 (d), 128.57 (d), 132.75 (d), 136.72 (s), 204.51 (s); GCMS *m/z* (rel intensity) 204 (M^+, 2), 134 (43), 105 (100), 77 (26), 41 (9); HRMS calcd for $C_{14}H_{20}O$ 204.1514, found 204.1519; FTIR (neat) 2932 (s), 1684 (vs), 1448 (m) cm^{-1}.

t. 4,4-Dimethyl-1,2-diphenyl-1-pentanone (39)



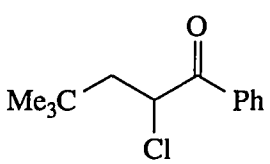
The compound was isolated as a white solid; ^{1}H NMR ($CDCl_3$) δ 0.884 (s, 9H), 1.58 (dd, 1H, *J*=3.3, 14.1 Hz), 2.63 (dd, 1H, *J*=9.0, 14.1 Hz), 4.72 (dd, 1H, *J*=3.3, 9.0 Hz), 7.13-7.53 (m, 8H), 7.97-8.02 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 29.83 (q), 31.19 (s), 47.59 (t), 49.66 (d), 126.70 (d), 128.09 (d), 128.54 (d, 2C), 128.86 (d), 132.71 (d), 137.02 (s), 141.09 (s), 199.91 (s); GCMS *m/z* (rel intensity) 266 (M^+, 1), 196 (11), 105 (100), 91 (39), 77 (29); HRMS calcd for $C_{19}H_{22}O$ 266.1671, found 266.1666; FTIR (neat) 3061 (w) 2955 (m), 2864 (w), 1672 (s) cm^{-1}.

u. 1,2-Diphenyl-1-heptanone (40)



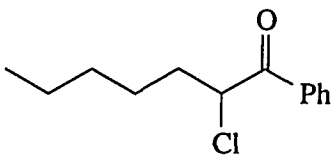
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.842 (t, 3H, *J*=6.9 Hz), 1.27 (m, 6H), 1.80 (m, 1H), 2.16 (m, 1H), 4.535 (t, 1H, *J*=7.2 Hz) 7.14-7.50 (m, 8H), 7.92-7.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.039 (q), 22.484 (t), 27.401 (t), 31.801 (t), 34.002 (t), 53.640 (d) 126.856 (d), 128.151 (d), 128.409 (d), 128.571 (d), 128.765 (d), 132.712 (d), 136.951 (s), 139.798 (s), 200.030 (s); GCMS *m/z* (rel intensity) 266 (M^+, 4), 196 (20), 105 (100), 91 (70), 77 (44); HRMS calcd for $C_{19}H_{22}O$ 266.1671, found 266.1675; FTIR (neat) 2930 (s), 1682 (vs), 1448 (m) cm^{-1}.

v. 2-Chloro-4,4-dimethyl-1-phenyl-1-pentanone (41)



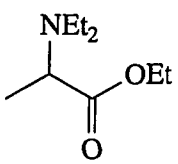
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.958 (s, 9H), 1.807 (dd, 1H, *J*=5.4, 14.4 Hz), 2.450 (dd, 1H, *J*=7.2, 14.4 Hz), 5.172 (dd, 1H, *J*=5.4, 7.2 Hz),7.46-7.54 (m, 2H), 7.57-7.64 (m, 1H), 8.01-8.05 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 29.9 (q), 31.0 (s), 46.5 (t), 53.6 (d), 128.8 (d), 128.9 (d), 133.7 (d), 134.4 (s), 193.5 (s); GCMS *m/z* (rel intensity) 224 (M^+, 1), 154 (3), 105 (100), 77 (22), 51 (6); HRMS calcd for $C_{13}H_{17}ClO$ 224.0968, found 224.0965; FTIR (neat) 2959 (m), 1695 (s) cm^{-1}.

w. 2-Chloro-1-phenyl-1-heptanone (42)



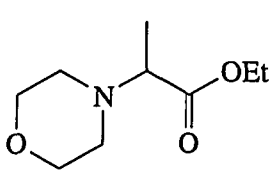
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.893 (t, 3H, *J*=3.0 Hz), 1.21-1.39 (m, 6H), 1.93-2.19 (m, 2H), 5.111 (dd, 1H, *J*=5.7, 8.1 Hz), 7.50 (m, 2H), 7.61 (m, 1H), 8.01 (m, 2H); GCMS *m/z* (rel intensity) 224 (M^+, 8), 154 (14), 106 (36), 77 (100), 51 (18); HRMS calcd for $C_{13}H_{17}ClO$ 224.0968, found 224.0968.

x. Ethyl 2-Diethylaminopropanoate (44)



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.040 (t, 6H, *J*=7.2 Hz), 1.251 (t, 3H, *J*=7.2 Hz), 1.269 (d, 3H, *J*=6.9 Hz), 2.40-2.80 (m, 4H), 3.524 (q, 1H, *J*=6.9 Hz), 4.15 (m, 2H).

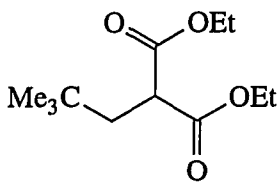
y. Ethyl 2-(4-Morpholino)propionate (46)



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.264 (t, 3H, *J*=7.2 Hz), 1.285 (d, 3H, *J*=6.9 Hz), 2.590 (t, 4H, *J*=3.9 Hz), 3.217 (q, 1H, *J*=6.9 Hz), 3.704

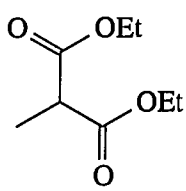
(t, 4H, *J*=3.9 Hz), 4.166 (q, 2H, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.33, 14.56, 49.92, 60.37, 62.93, 67.13, 172.7; GCMS *m/z* (rel intensity) 187 (M^+, 4), 115 (12), 114 (100), 70 (14), 56 (13); HRMS calcd for $C_9H_{17}NO_3$ 187.1208, found 187.1206.

z. Diethyl 2,2-Dimethylpropylmalonate (48)



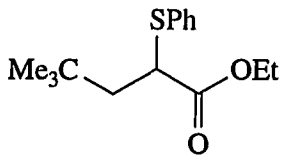
The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.891 (s, 9H), 1.240 (t, 6H, *J*=7.2 Hz), 1.918 (d, 2H, *J*=6.3 Hz), 3.370 (t, 1H, *J*=6.0 Hz), 4.163 (m, 4H); GCMS *m/z* (rel intensity) 231 (M^++1, 0.5), 215 (20),185 (38), 174 (33), 141 (54), 128 (86), 101 (65), 73 (39), 57 (100), 55 (46), 41 (80).

aa. Diethyl Methylmalonate (49)



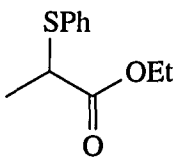
The compound was isolated and identified by comparison of its ^1H NMR with the authentic sample; ^1H NMR ($CDCl_3$) δ 1.238 (t, 6H, *J*=7.2 Hz), 1.405 (d, 3H, *J*=7.2 Hz), 3.402 (q, 1H, *J*=7.2 Hz), 4.171 (dq, 4H, *J*=1.5, 7.2 Hz); GCMS *m/z* (rel intensity) 174 (M^+, 11), 147 (17), 129 (87), 102 (33), 74 (100), 57 (60), 56 (66), 45 (37), 41 (21).

bb. Ethyl 4,4-Dimethyl-2-phenylmercaptopentanoate (50)



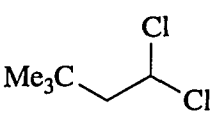
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.908 (s, 9H), 1.104 (t, 3H, *J*=7.2 Hz), 1.610 (dd, 1H, *J*=2.7, 14.1 Hz), 2.081 (dd, 1H, *J*=10.2, 14.1 Hz), 3.713 (dd, 1H, *J*=3.0, 10.8 Hz), 4.024 (q, 1H, *J*=7.2 Hz), 4.030 (q, 1H, *J*=7.2 Hz), 7.27-7.33 (m, 3H), 7.45-7.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.88 (q), 29.21 (q), 31.25 (s), 45.46 (t), 47.46 (d), 60.92 (t), 128.0 (d), 128.8 (d), 133.1 (d), 133.5 (s), 172.9 (s); GCMS *m/z* (rel intensity) 266 (M^+, 60), 193 (38), 137 (100), 110 (16), 109 (22), 77 (22); HRMS calcd for $C_{15}H_{22}O_2S$ 266.1345, found 266.1340.

cc. Ethyl 2-Phenylthiopropionate (51)



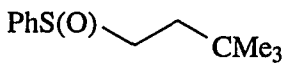
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.171 (t, 3H, *J*=7.2 Hz), 1.482 (d, 3H, *J*=7.2 Hz), 3.786 (q, 1H, *J*=7.2 Hz), 4.110 (q, 2H, *J*=7.2 Hz), 7.28 (m, 3H), 7.45 (m, 2H).

dd. 1,1-Dichloro-3,3-dimethylbutane[82] (52)



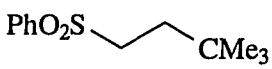
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 9H), 2.26 (d, 2H, *J*=6.0 Hz), 5.80 (t, 1H, *J*=6.0 Hz).

ee. 3,3-Dimethylbutyl Phenyl Sulfoxide[83] (53)



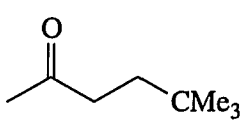
The compound was identified by ^{1}H NMR and confirmed by comparison of the spectral data with the literature; ^{1}H NMR ($CDCl_3$) δ 0.876 (s, 9H), 1.50-1.64 (m, 2H), 2.68-2.87 (m, 2H), 7.45-7.75 (m, 5H).

ff. 3,3-Dimethylbutyl Phenyl Sulfone[84] (54)



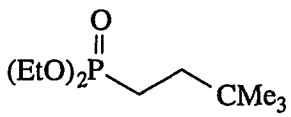
The compound was isolated as a solid, mp 56-58 °C; ^{1}H NMR ($CDCl_3$) δ 0.863 (s, 9H), 1.599 (m, 2H), 3.058 (m, 2H), 7.53-7.60 (m, 2H), 7.62-7.66 (m, 1H), 7.88-7.94 (m, 2H); GCMS *m/z* (rel intensity) 226 (M^+, 2), 169 (14), 161 (13), 143 (54), 142 (16), 105 (6), 85 (14), 77 (19), 69 (26), 57 (100), 55 (11); HRMS calcd for $C_{12}H_{18}O_2S$ 226.1028, found 226.1031.

gg. 5,5-Dimethyl-2-hexanone[85] (55)



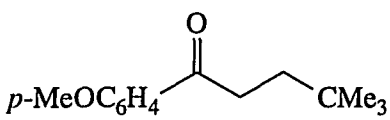
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.886 (s, 9H), 1.486 (t, 2H, *J*-7.8 Hz), 2.147 (s, 3H), 2.389 (t, 2H, *J*=7.8 Hz).

hh. Diethyl 3,3-Dimethylbutylphosphonate[24] (56)



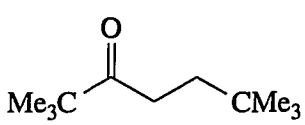
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.891 (s, 9H), 1.325 (t, 6H, *J*=7.2 Hz), 1.39-1.53 (m, 2H), 1.62-1.76 (m, 2H), 4.09 (m, 4H); ^{13}C NMR δ 16.41, 21.20, 28.68, 29.37, 35.80, 61.37; GCMS *m/z* (rel intensity) 222 (M^+, 0.2), 207 (49),166 (58), 165 (100), 151 (52), 138 (96), 111 (63), 57 (66); HRMS calcd for $C_{10}H_{22}O_3P$ (M^+-1) 221.1306, found 221.1304.

ii. 4,4-Dimethyl-1-(4-methoxyphenyl)-1-pentanone (58)



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.955 (s, 9H), 1.624 (t, 2H, *J*=8.4 Hz), 2.880 (t, 2H, *J*-8.4 Hz), 3.864 (s, 3H), 6.932 (m, 2H), 7.945 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 29.19, 30.20, 33.94, 38.37, 55.39, 113.6, 130.0, 130.3, 163.2, 199.6; GCMS *m/z* (rel intensity) 220 (M^+, 12), 205 (9), 163 (18), 150 (11), 135 (100), 107 (8), 77 (12), 57 (3); HRMS calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1464.

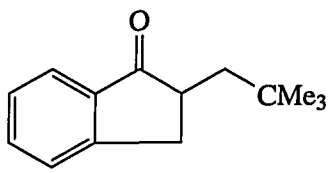
jj. 2,2,6,6-Tetramethyl-3-heptanone[86] (60)



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.890 (s, 9H), 1.147 (s, 9H), 1.447 (t, 2H, *J*=8.1 Hz), 2.436 (t, 2H, *J*=8.1 Hz); GCMS *m/z* (rel intensity) 170

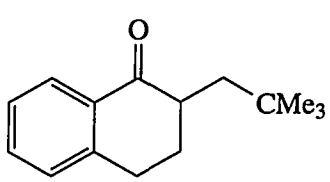
(M^+, 6), 113 (13), 85 (18), 57 (100); HRMS calcd for $C_{11}H_{22}O$ 170.1671, found 170.1666.

kk. 2-(2,2-Dimethylpropyl)-1-indanone (62)



The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 1.014 (s, 9H), 1.236 (dd, 1H, *J*=10.8, 13.8 Hz), 2.108 (dd, 1H, *J*=1.5, 13.8 Hz), 2.602 (m, 1H), 2.838 (dd, 1H, *J*=3.9, 17.1 Hz), 3.433 (dd, 1H, *J*=7.8, 17.1 Hz), 7.348 (m, 1H), 7.439 (d, 1H, *J*=7.5 Hz), 7.568 (m, 1H), 7.748 (d, 1H, *J*=7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 29.89 (q), 30.93 (s), 36.12 (t), 45.07 (d), 45.71 (t), 123.8 (d), 126.3 (d), 127.2 (d), 134.5 (d), 136.4 (s), 153.7 (s), 209.3 (s); GCMS *m/z* (rel intensity) 202 (M^+, 10), 187 (8), 145 (100), 131 (12), 117 (17), 91 (6), 57 (10); HRMS calcd for $C_{14}H_{18}O$ 202.1358, found 202.1363.

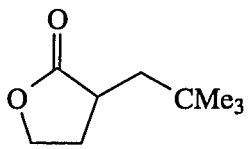
ll. 2-(2,2-Dimethylpropyl)-1-tetralone (64)



The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.959 (s, 9H), 1.087 (dd, 1H, *J*=5.1, 14.1 Hz), 1.963 (m, 1H), 2.246 (m, 2H), 2.452 (m, 1H), 2.996 (m, 2H), 7.221 (d, 1H, *J*=7.2 Hz), 7.286 (m, 1H), 8.015 (d, 1H, *J*=7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 28.68, 29.61, 30.92, 31.71, 42.48, 44.67, 126.4, 127.5, 128.6, 132.6,

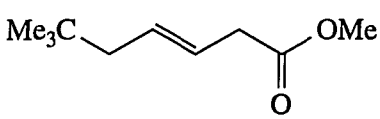
132.9, 143.7, 200.6; GCMS *m/z* (rel intensity) 216 (M^+, 12), 202 (2), 201 (13), 160 (16), 159 (100), 145 (21), 118 (12), 90 (10); HRMS calcd for $C_{15}H_{20}O$ 216.1514, found 216.1508.

mm. Dihydro-3-(2,2-Dimethylpropyl)-2(3*H*)-furanone (65)



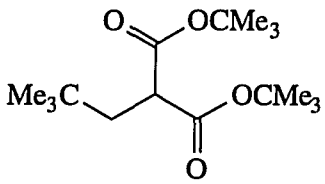
The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.958 (s, 9H), 1.274 (dd, 1H, *J*=9.9, 14.4 Hz), 1.959 (m, 1H), 2.026 (dd, 1H, *J*=1.8, 14.4 Hz), 2.507 (m, 2H), 4.157 (m, 1H), 4.342 (m, 1H); GCMS *m/z* (rel intensity) 157 (M^++1, 47), 141 (25), 100 (61), 99 (69), 95 (12), 69 (24), 67 (13), 57 (69), 56 (16), 55 (89), 53 (13), 43 (19), 41 (100), 39 (68); HRMS calcd for $C_8H_{13}O_2$ (M^+-CH_3) 141.0916, found 141.0918.

nn. Methyl 6,6-Dimethyl-3-heptenoate[87] (67)



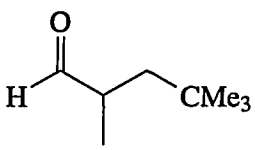
The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.872 (s, 9H), 1.914 (d, 2H, *J*=6.9 Hz), 3.057 (d, 2H, *J*=6.3 Hz), 3.681 (s, 3H), 5.44-5.54 (td, 1H, *J*=6.3, 15.0 Hz), 5.54-5.64 (td, 1H, *J*=6.9, 15.0 Hz); GCMS *m/z* (rel intensity) 170 (M^+, 1), 155 (9), 113 (54), 95 (16), 85 (14), 69 (33), 68 (14), 57 (73), 56 (11), 55 (28), 43 (26), 41 (100), 39 (62); HRMS calcd for $C_{10}H_{18}O_2$ 170.1307, found 170.1302.

oo. Bis(1,1-dimethylethyl) 2,2-Dimethylpropylmalonate (69)



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.898 (s, 9H), 1.455 (s, 18H), 1.829 (d, 2H, *J*=6.0 Hz), 3.174 (t, 1H, *J*=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 27.89 (q), 29.25 (q), 30.41 (s), 41.67 (t), 50.83 (d), 81.14 (s), 169.6 (s); HRMS calcd for $C_{12}H_{21}O_3$ (M^+-$OCMe_3$) 213.1491, found 213.1486.

pp. 2,4,4-Trimethylpentaldehyde[88] (70)



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.906 (s, 9H), 1.093 (d, 3H, *J*=7.2 Hz), 1.160 (dd, 1H, *J*=10.5, 14.4 Hz); 1.823 (dd, 1H, *J*=7.5, 14.4 Hz), 2.414 (m, 1H), 9.551 (d, 1H, *J*=3.0 Hz).

CHAPTER II. KINETIC CHAIN LENGTH AND RELATIVE REACTIVITIES OF SUBSTITUTED OLEFINS TOWARDS *TERT*-BUTYL RADICAL

A. Initial Kinetic Chain Length

Chemical kinetics and its supporting techniques have proven to be valuable approaches to the study of reaction mechanisms and to an understanding of chemical reactivity. A chain reaction is one in which the mechanism involves low concentrations of reactive intermediates (chain carriers) that participate in a cycle of reaction steps such that intermediates are regenerated after each cycle. Chain carriers are formed in a chain initiation step and participate in chain propagation steps which can be interrupted by a termination step.

Kinetic chain length represents the average number of reaction molecules consumed for every radical which initiates a chain reaction.[89] Ultimately the initiation reaction must produce stable products via a number of chain propagation steps.[90] Therefore, the magnitude of a kinetic chain length can be a criterion to determine whether the reaction is a chain process or not. To calculate the kinetic chain length, the rate of the chain initiation must be known. This rate can be conveniently measured from the inhibition period observed with known amounts of free radical scavengers. Free radical chain reactions are commonly susceptible to inhibition in which a small amount of a radical scavenger can cause a marked retardation for either the formation of the reaction product or the consumption of the coreactant which is added to form a radical addition product.

B. Relative Reactivity

Because of the difficulty in determining the absolute rate constants of chain propagation steps efficiently and accurately, the number of chain reactions for which complete information is known is still quite limited. However, one is often interested in and satisfied with knowing relative rates of the reaction of some radical R• with two substances A_1 and A_2 to give products P_1 and P_2.[90,91] If the rate constant is known for one of the substances, the absolute rate constant of the other substance can be calculated from relative reactivity data. In the direct competitive approach, one needs to design an experimental system in which the radical R• can be generated in a mixture of A_1 and A_2. When the radical R• is generated in a mixture of substances A_1 and A_2, both of which react with the radical R•, the following equation can be derived for determining the relative reactivity.

$$\begin{aligned} A_1 + R^\bullet &\xrightarrow{k_1} P_1 \\ A_2 + R^\bullet &\xrightarrow{k_2} P_2 \end{aligned} \qquad (30)$$

Since $d[P_1]/dt = k_1[A_1][R^\bullet]$

$$d[P_2]/dt = k_2[A_2][R^\bullet] \qquad (31)$$

Division gives $$d[P_1]/d[P_2] = (k_1/k_2)([A_1]/[A_2]) \qquad (32)$$

Equation 32 may be considered in two cases:

a) The case when $[A_1]$ and $[A_2] >> [P]$, i.e. reactants are in large excess and their concentration are then effectively constant, in which case the product ratio gives the rate constant ratio by following equation.

$$k_1/k_2 = [P_1]_\infty[A_2]_o/[P_2]_\infty[A_1]_o$$

$$k_1/k_2 = [P_1]_\infty/[P_2]_\infty \qquad (\text{if } [A_1]_o = [A_2]_o) \qquad (33)$$

Equation 33 can be used to calculate the rate ratio of two reactants when the two reactants are used in large excess.

b) When the concentrations of reactants $[A_1]$ and $[A_2]$ do not remain constant during the course of the experiment, the relative reactivities can be obtained by integration between the limits of initial and final concentrations of $[A_1]$ and $[A_2]$. Since $[A]_o = [A]_f + [P]_f$, this yields

$$k_1/k_2 = \ln\{[A_1]_o/([A_1]_o - [P_1]_f\}/\ln\{[A_2]_o/([A_2]_o - [P_2]_f)\} \qquad (34)$$

Equation 34 can be used to calculate relative reactivity of the two reactants when the radical processor is in large excess and reaction is quenched before its completion, i.e., before one of the reagents A_1 or A_2 is completely consumed.

In this chapter, results will be presented on the determination of the kinetic chain length for the *tert*-butylation of ethyl methacrylate with silane system and the reaction between 3,3-diacetylpropylmercuric chloride and diphenyl disulfide with irradiation. Results will also be presented and discussed for the measurement of relative reactivities of various substances towards *tert*-butyl radical and substituent effects on the reactivities of olefins.

C. Results and Discussion

1. Initial Kinetic Chain Length of the *tert*-Butylation of Ethyl Methacrylate in the Presence of Triethylsilane

The kinetic chain length (k.c.l.) of a reaction can be formulated as shown in equation 35.

$$\text{k.c.l.} = \frac{\text{Initial reaction rate}}{\text{Rate of initiation}} \qquad (35)$$

The initial reaction rate can be measured experimentally by following either the rate of the consumption of the substrate or the rate of the formation of the product. The rate of the initiation can also be determined by measuring the inhibition period in the presence of a small amount of a radical inhibitor [usually 10 mol% of di-*tert*-butyl nitroxide (DTBN) is used as the radical scavenger]. The progress of the reaction can be conveniently monitored by ^{1}H NMR spectroscopy in solution such as deuterated dimethyl sulfoxide.

The kinetic chain length of the reaction between ethyl methacrylate and *tert*-butylmercury chloride in the presence of triethylsilane was determined by measuring the initial reaction rate and the rate of initiation process with ^{1}H NMR spectroscopy in Me_2SO-d_6. Two identical NMR tube reaction mixtures were prepared and analyzed alternately. Data are presented in Table XXVI and Figure II.

From Figure II, the initial reaction rate is estimated as 0.036C M/min and the rate of initiation as 0.0045C M/min (C is initial concentration of ethyl methacrylate). The initial kinetic chain length calculated is 8.

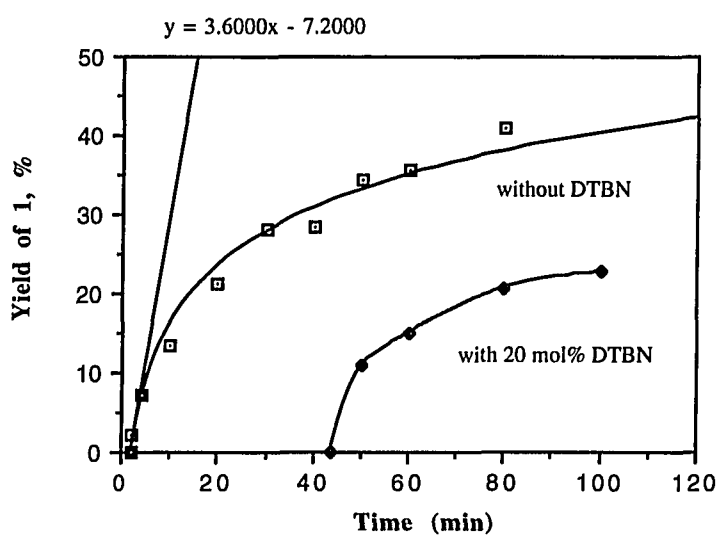
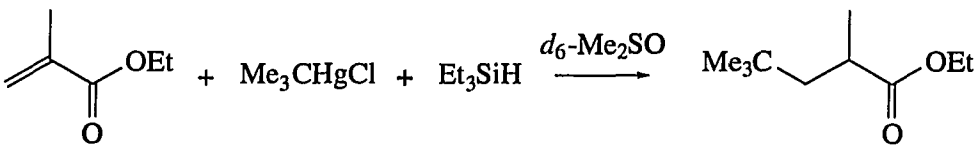


Figure II. Yield of Product **1** with Time

Table XXVI. *tert*-Butylation of Ethyl Methacrylate in the Presence of Et_3SiH[a]



1

Entry	Time (min)	Yield of Product **1**, %	
		without DTBN	with DTBN[b]
1	2	2.3	0.0
2	10	13.4	0.0
3	20	21.2	0.0
4	30	28.0	0.0
5	40	28.5	0.0
6	50	34.5	10.9
7	60	35.6	15.0
8	80	41.0	20.6
9	100		22.7

[a]Reaction of 0.1 mmol of ethyl methacrylate with 2 equiv. of Me_3CHgCl and Et_3SiH in 0.6 mL of deuterated dimethyl sulfoxide in the dark.
[b]20 mol% based on ethyl methacrylate.

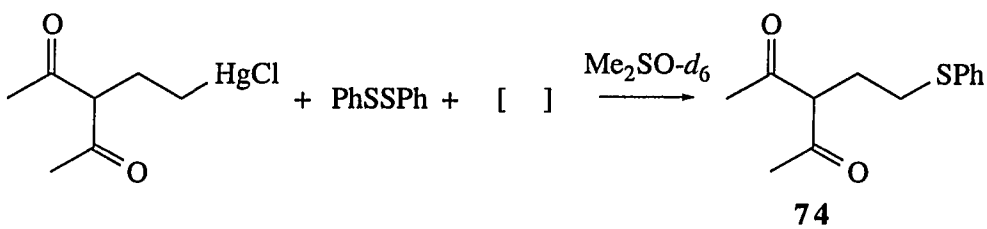
2. Initial Kinetic Chain Length of the Reaction of 3,3-Diacetylpropylmercuric Chloride with PhSSPh under Irradiation

The kinetic chain length of the photostimulated reaction between 3,3-diacetylpropylmercuric chloride and diphenyl disulfide was also determined by measuring the initial reaction rate and the rate of the initiation process with ^1H NMR spectroscopy. Although addition of potassium iodide dramatically improved the product yield, the *tert*-butyl nitroxide inhibition experiment was carried out without it for the consideration of

measurement accuracy. Two identical NMR tube reaction mixtures were prepared and analyzed alternately by ^1H NMR. Data are presented in Table XXVII and Figure III.

From Figure III, the initial reaction rate is estimated as 0.00225 M/min and the rate of initiation as 0.00007 M/min. The kinetic chain length calculated is 32.

Table XXVII. Reaction of 3,3-Diacetylpropylmercuric Chloride with PhSSPh[a]



74

Entry	Time (min)	Yield of the Product **74**, %		
		with KI	without KI and DTBN	with DTBN[b]
1	10	33.0	17.5	0.0
2	40	70.0	35.5	0.0
3	60		40.0	0.0
4	90		43.8	0.0
5	120		47.4	0.0
6	150		50.0	12.2
7	160			19.6
8	170			26.5
9	180		52.3	31.0
10	240		56.0	43.5

[a]Reaction of 0.1 mmol of 3,3-Diacetylpropylmercuric Chloride and PhSSPh in 1.0 mL of Me_2SO-d_6 with 275 W fluorescent sunlamp irradiation at *ca.* 35 °C.
[b]10 mol% based on 3,3-Diacetylpropylmercuric Chloride.

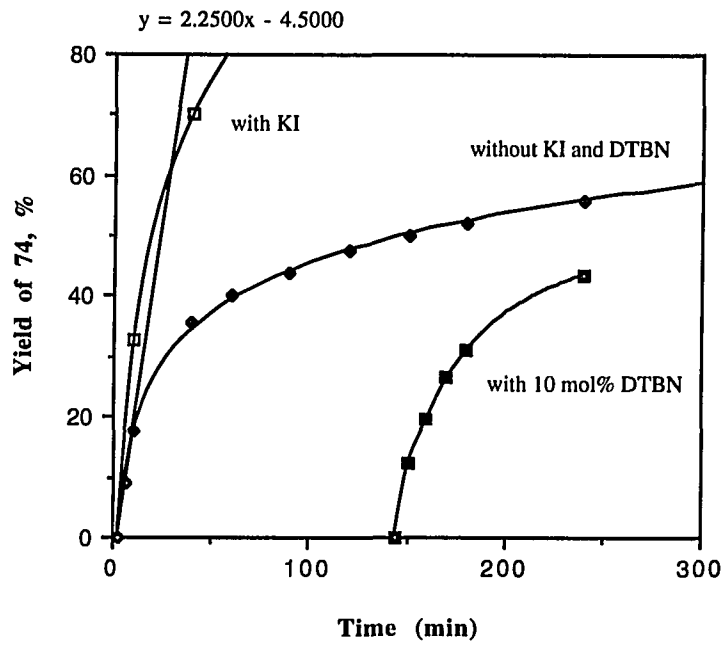


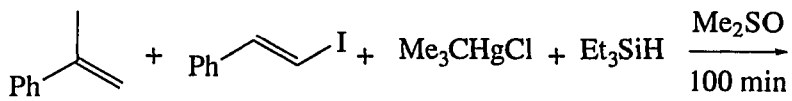
Figure III. Yield of Product **74** with Time

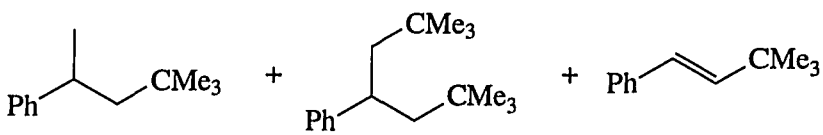
3. Relative Reactivities of Various Compounds toward *tert*-Butyl Radical Measured by the Silyl Hydride Method

Competition reactions between two substrates which individually react with tert-butylmercury chloride in the presence of triethylsilane by a chain process yield relative reactivity data concerning the product determining steps. Although the reaction is a fairly short chain process, product formation is determined only by the irreversible addition of the *tert*-butyl radical to the competing substrates. Therefore, the relative reactivity of the two substrates towards *tert*-butyl radical is reflected by the product ratio. Most of the competition reactions were conducted with an excess amount of *tert*-butylmercury chloride and the rate ratios were calculated using equation 34. For this method, typically 0.1 mmol of each substrate, 0.4 mmol of *tert*-BuHgCl, and 0.4 mmol of Et_3SiH were used. The ^1H

NMR and GC yields were determined with toluene (0.1 mmol) as an added internal standard. Results are presented in following equations for the measurement of relative reactivities of each pair of substrates. The reaction of (E)-β-iodostyrene with *tert*-butylmercury chloride to yield (E)-(3,3-dimethylbutenyl)benzene was used where possible as a standard reaction with which to compare the reactivity of the various substituted alkenes. Relative reactivity data are summarized in Table XXVIII (page 113).

a. α-Methylstyrene and (E)-β-Iodostyrene

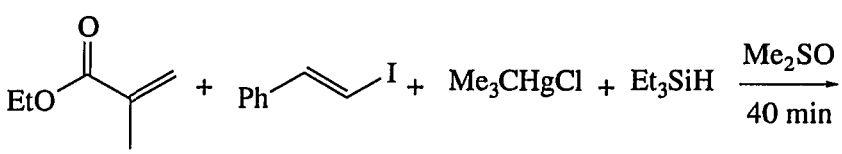


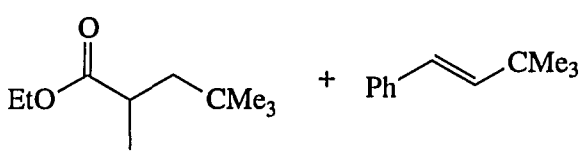


11.3% 4.7% 5.9%

k_1/k_2
2.9

b. Ethyl Methacrylate and (E)-β-Iodostyrene

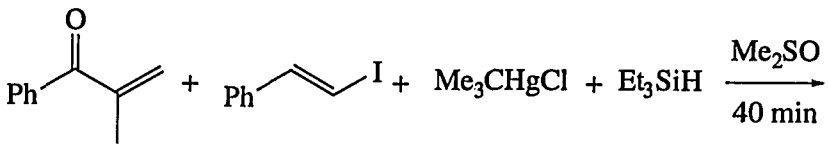


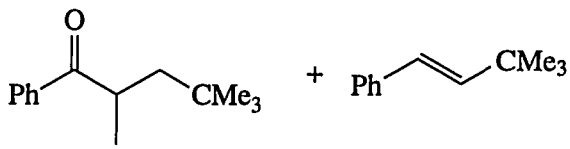


64% 1.7%

k_1/k_2
60

c. Phenyl 2-Propenyl Ketone and (E)-β-Iodostyrene

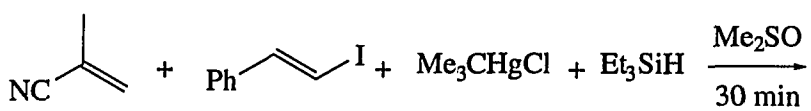


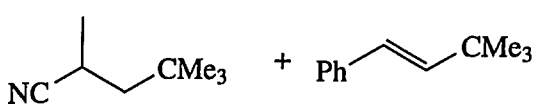


69% 1.6%

k_1/k_2
73

d. Methacrylonitrile and (E)-β-Iodostyrene

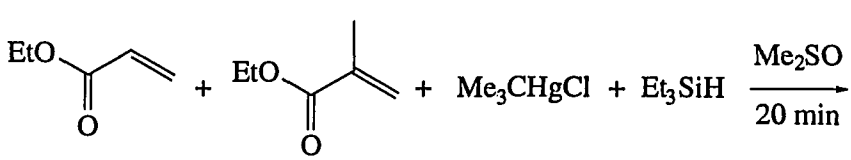


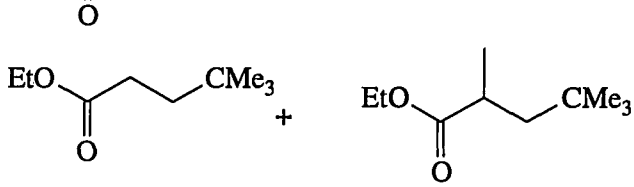


34% 0.7%

k_1/k_2
59

e. Ethyl Acrylate and Ethyl Methacrylate

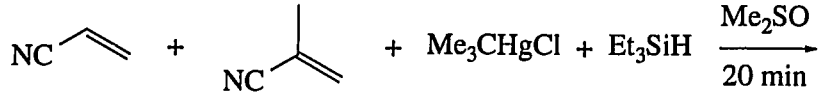


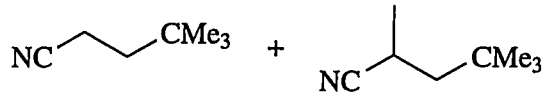


33% 24%

k_1/k_2
1.46

f. Acrylonitrile and Methacrylonitrile

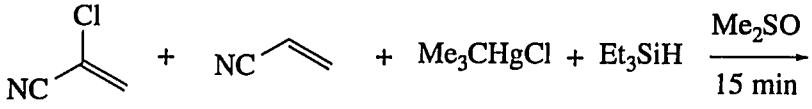


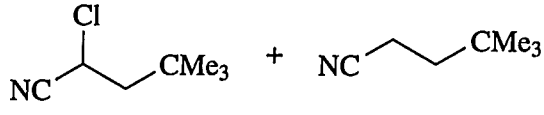


49% 16%

k_1/k_2
3.9

g. α-Chloroacrylonitrile and Acrylonitrile

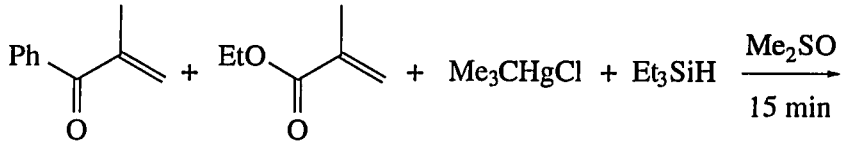


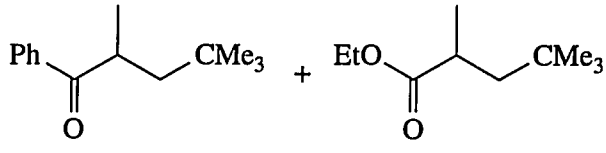


49% 13%

k_1/k_2
4.7

h. Phenyl 2-Propenyl Ketone and Ethyl Methacrylate

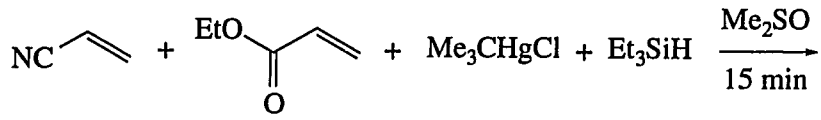


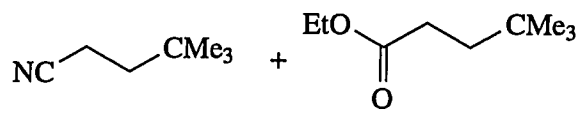


39% 33%

k_1/k_2
1.2

i. Acrylonitrile and Ethyl Acrylate

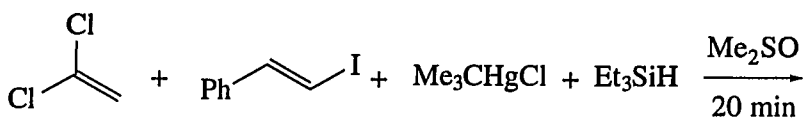


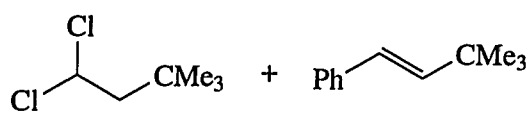


40% 18%

k_1/k_2
2.57

j. Vinylidene Chloride and (E)-β-Iodostyrene

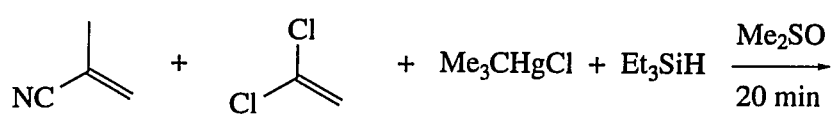


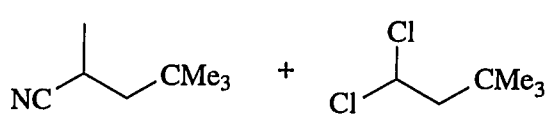


35% 2.7%

k_1/k_2
15.7

k. Methacrylonitrile and Vinylidene Chloride

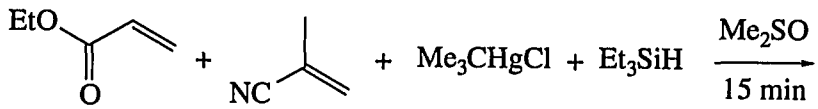


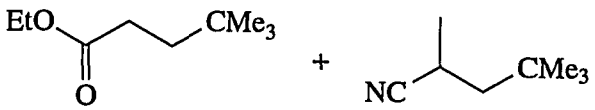


37% 7.3%

k_1/k_2
6.1

l. Ethyl Acrylate and Methacrylonitrile

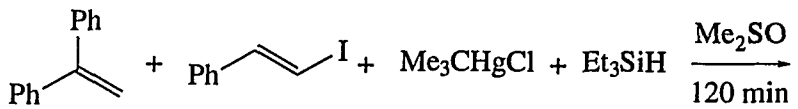


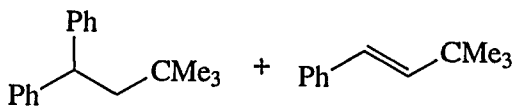


20% 13%

k_1/k_2
1.6

m. 1,1-Diphenylethylene and (E)-β-Iodostyrene

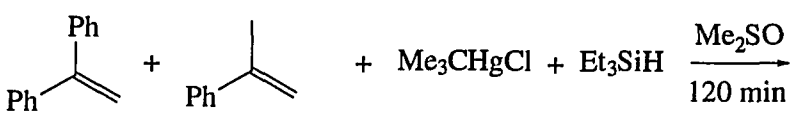


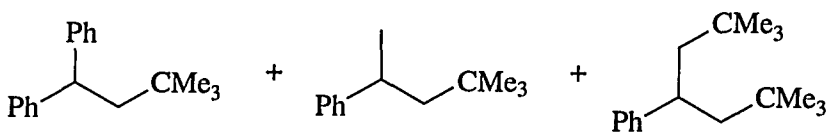


13.6% 0.6%

k_1/k_2
24

n. 1,1-Diphenylethylene and α-Methylstyrene

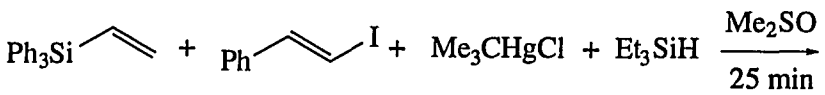


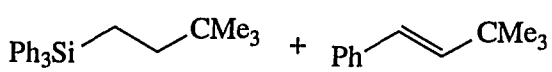


11.6% 0.74% 0.49%

k_1/k_2
10

o. Triphenylvinylsilane and (E)-β-Iodostyrene

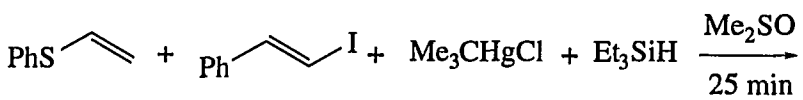


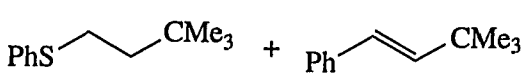


24% 15.7%

k_1/k_2
1.61

p. Phenyl Vinyl Sulfide and (E)-β-Iodostyrene

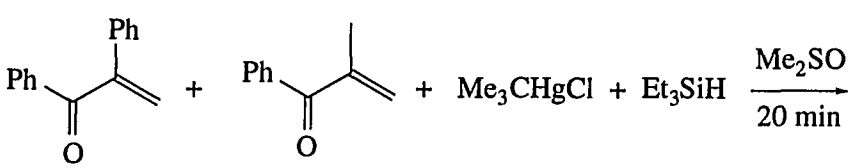


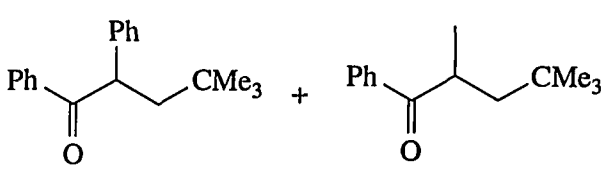


14.5% 3.8%

k_1/k_2
4.04

q. α-Methylene Deoxybenzoin and Phenyl 2-Propenyl Ketone

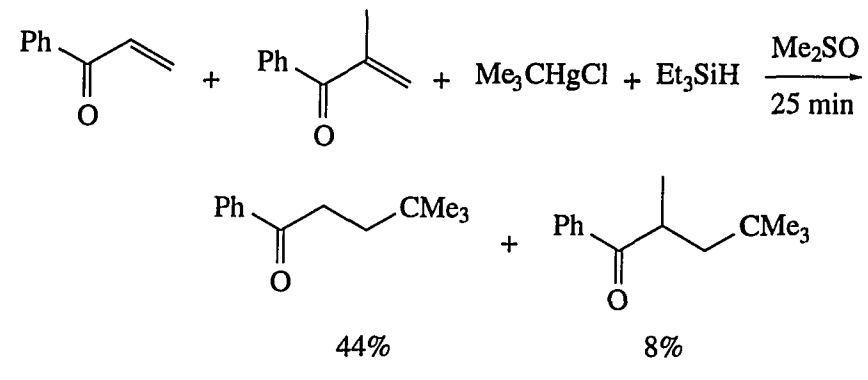




21% 8.4%

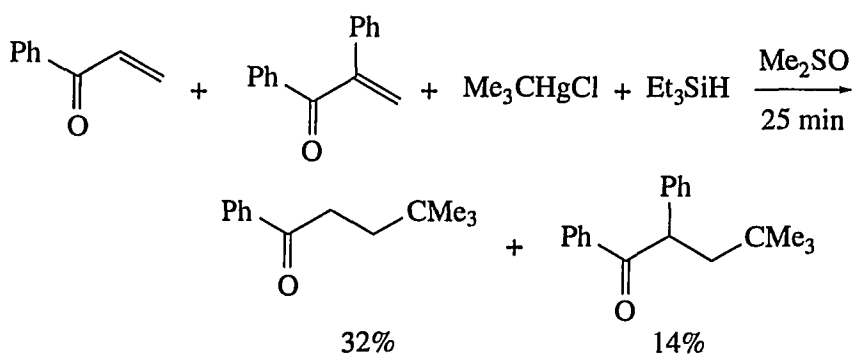
k_1/k_2
2.7

r. Phenyl Vinyl Ketone and Phenyl 2-Propenyl Ketone



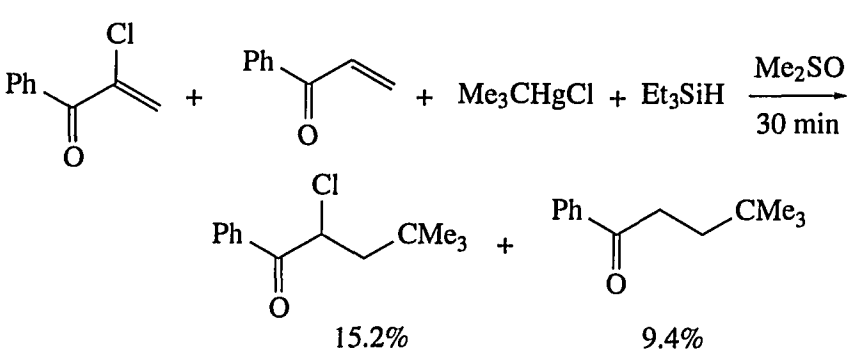
k_1/k_2
6.9

s. Phenyl Vinyl Ketone and α-Methylene Deoxybenzoin



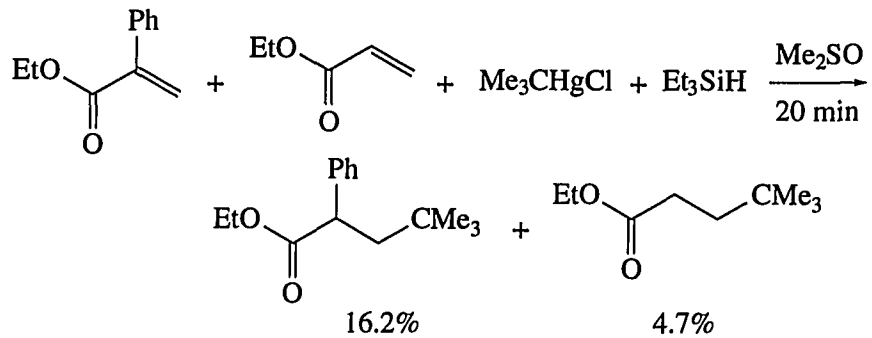
k_1/k_2
2.56

t. 1-Chlorovinyl Phenyl Ketone and Phenyl Vinyl Ketone



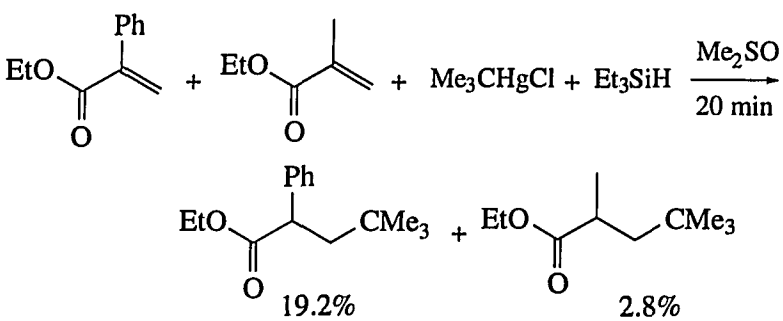
k_1/k_2
1.67

u. Ethyl α-Phenylacrylate and Ethyl Acrylate



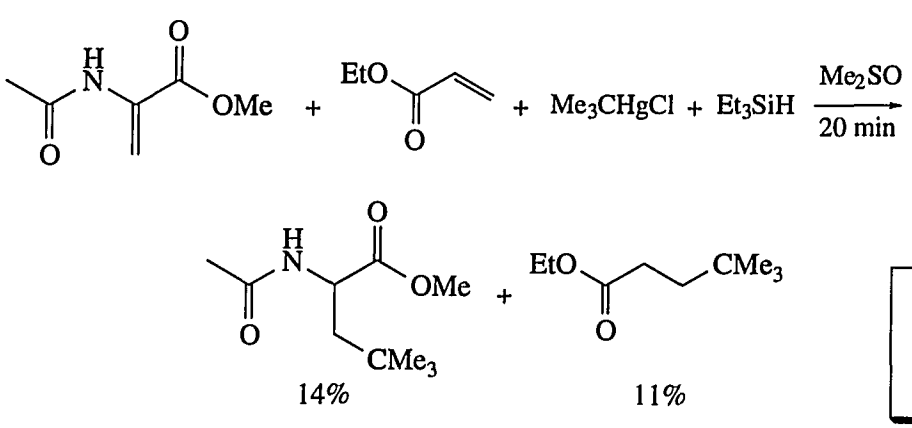
k_1/k_2
3.7

v. Ethyl α-Phenylacrylate and Ethyl Methacrylate



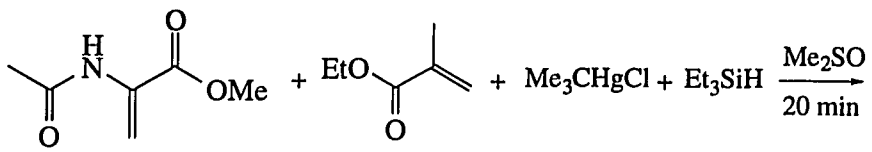
k_1/k_2
7.5

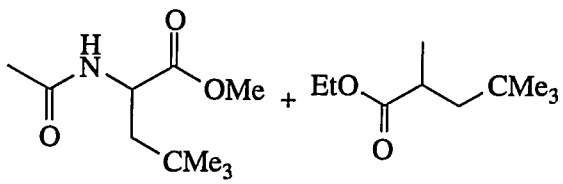
w. Methyl 2-Acetamidoacrylate and Ethyl Acrylate



k_1/k_2
1.3

x. Methyl 2-Acetamidoacrylate and Ethyl Methacrylate

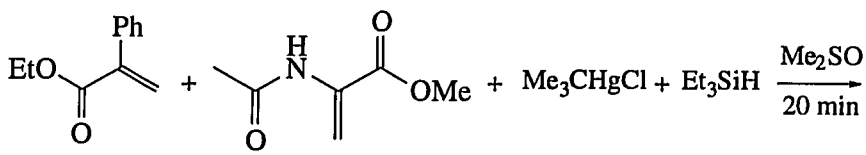


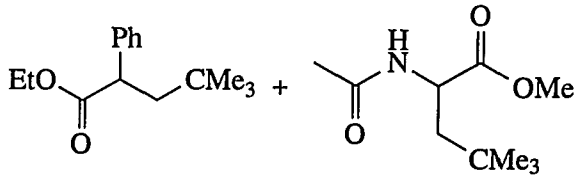


15.6% 8.1%

k_1/k_2
2.0

y. Ethyl α-Phenylacrylate and Methyl 2-Acetamidoacrylate

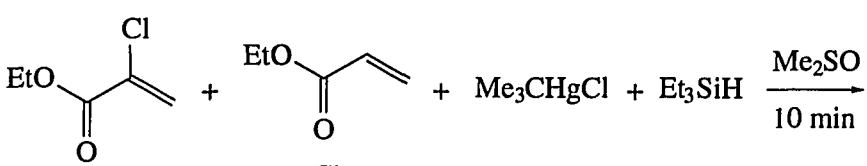


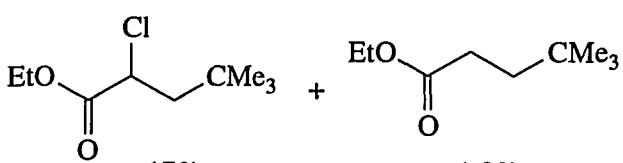


14% 5.2%

k_1/k_2
2.8

z. Ethyl α-Chloroacrylate and Ethyl Acrylate

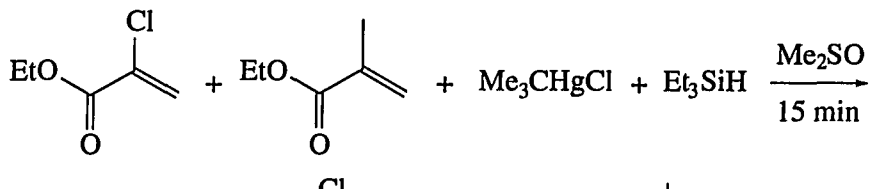


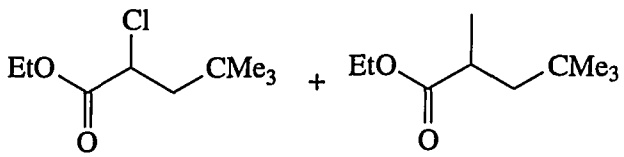


17% 1.0%

k_1/k_2
18

aa. Ethyl α-Chloroacrylate and Ethyl Methacrylate

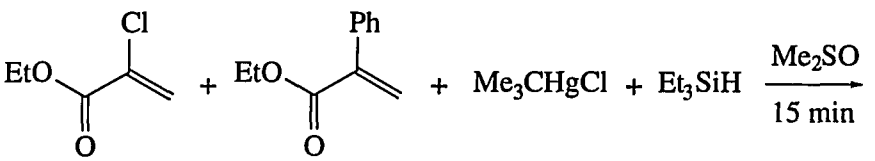


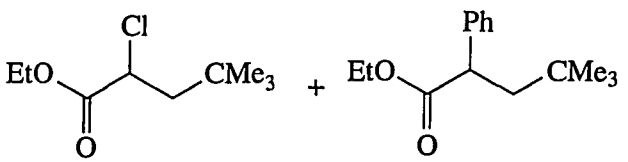


22% 1.1%

k_1/k_2
22

bb. Ethyl α-Chloroacrylate and Ethyl α-Phenylacrylate

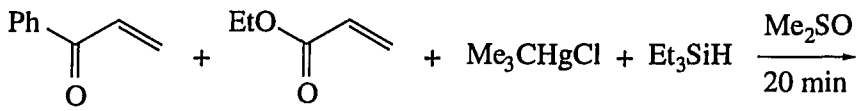


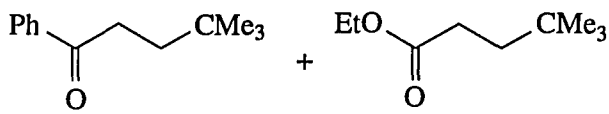


15% 4.8%

k_1/k_2
3.3

cc. Phenyl Vinyl Ketone and Ethyl Acrylate

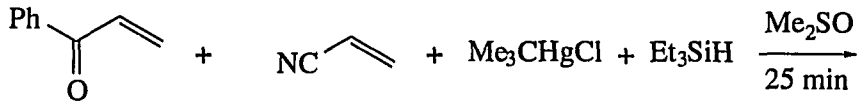


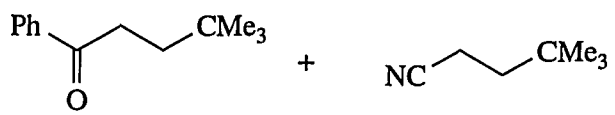


41% 11%

k_1/k_2
4.5

dd. Phenyl Vinyl Ketone and Acrylonitrile

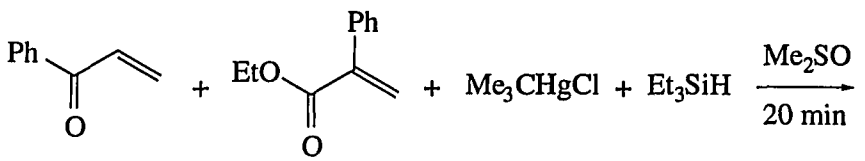


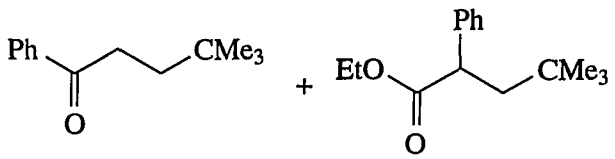


35% 22%

k_1/k_2
1.7

ee. Phenyl Vinyl Ketone and Ethyl α-Phenylacrylate

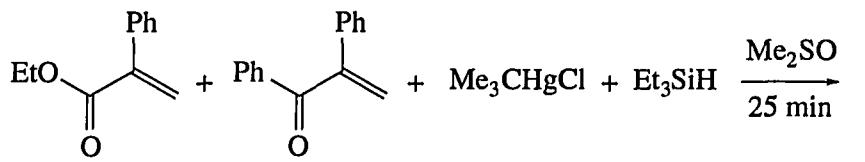


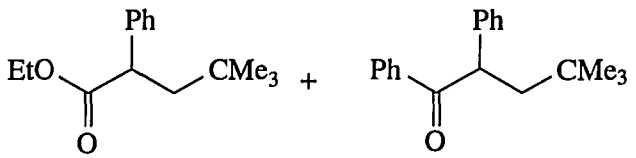


25% 14%

k_1/k_2
1.9

ff. Ethyl α-Phenylacrylate and α-Methylene Deoxybenzoin

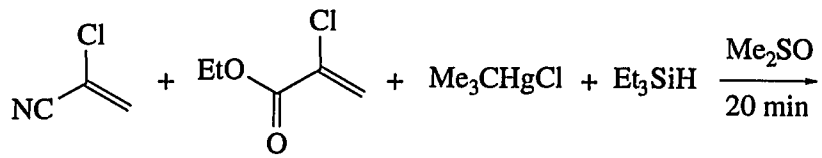


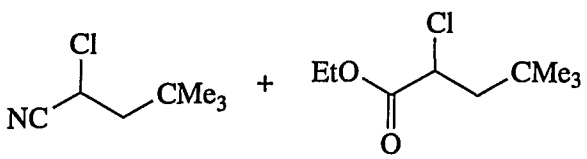


21% 12%

k_1/k_2
1.8

gg. α-Chloroacrylonitrile and Ethyl α-Chloroacrylate

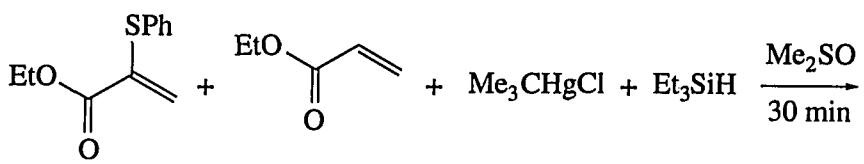


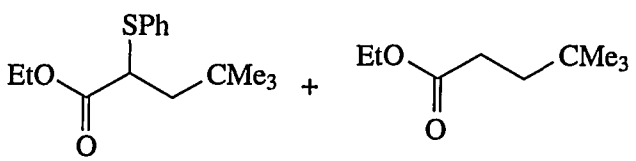


19% 13%

k_1/k_2
1.5

hh. Ethyl α-(Phenylthio)acrylate and Ethyl Acrylate

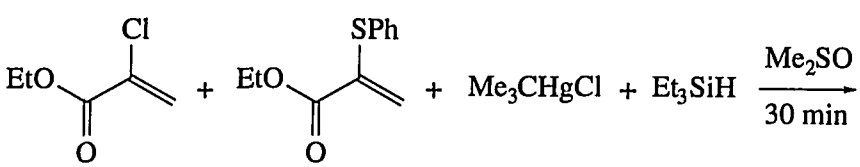


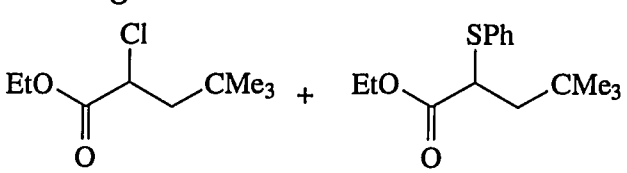


14% 5.8%

k_1/k_2
2.5

ii. Ethyl α-Chloroacrylate and Ethyl α-(Phenylthio)acrylate

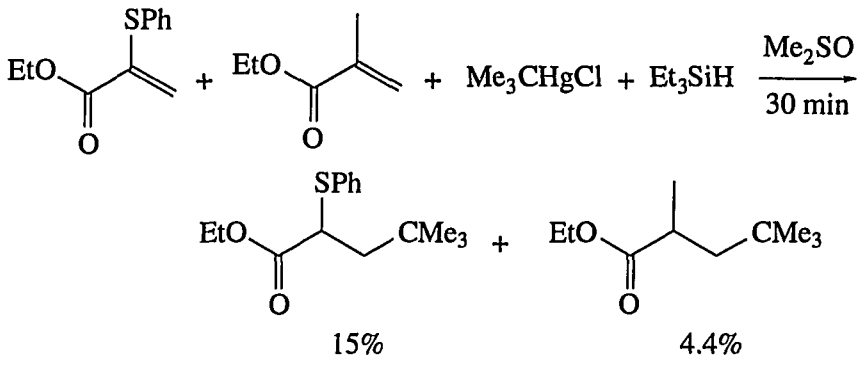




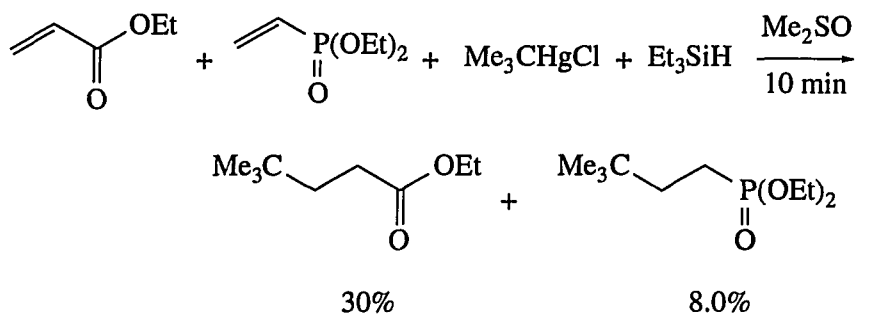
24.3% 7.6%

k_1/k_2
3.5

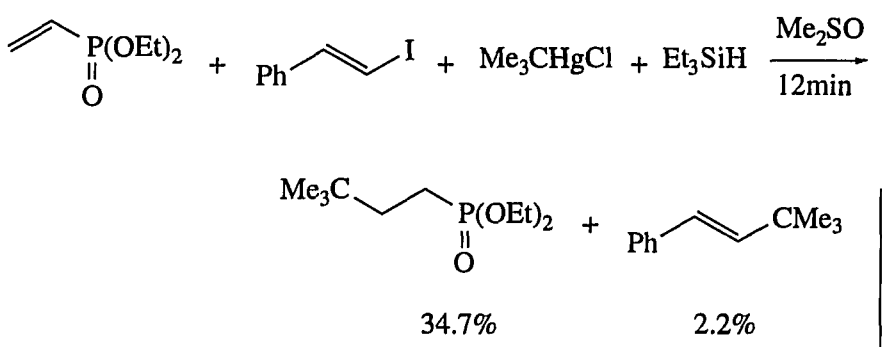
jj. Ethyl α-(Phenylthio)acrylate and Ethyl Methacrylate



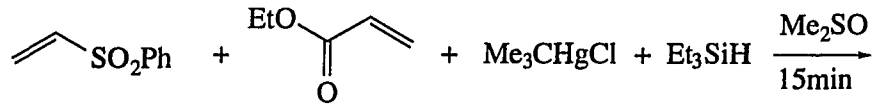
kk. Ethyl Acrylate and Diethyl Vinylphosphonate

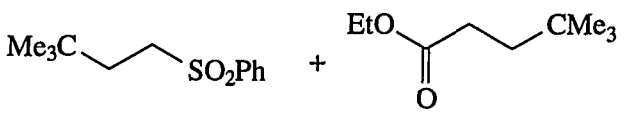


ll. Diethyl Vinylphosphonate and (E)-β-Iodostyrene



mm. Phenyl Vinyl Sulfone and Ethyl Acrylate

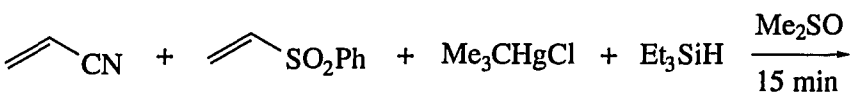




18.1% 16.9%

k_1/k_2
1.1

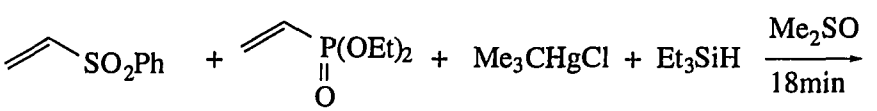
nn. Acrylonitrile and Phenyl Vinyl Sulfone

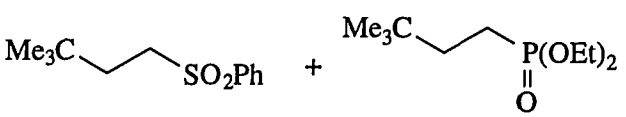


24.4% 8.0%

k_1/k_2
3.4

oo. Phenyl Vinyl Sulfone and Diethyl Vinylphosphonate

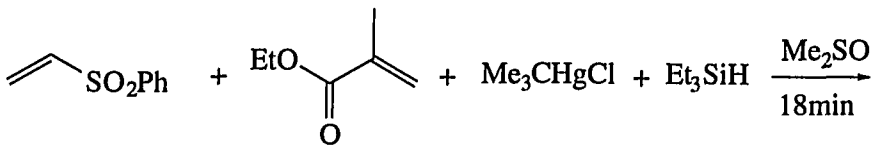


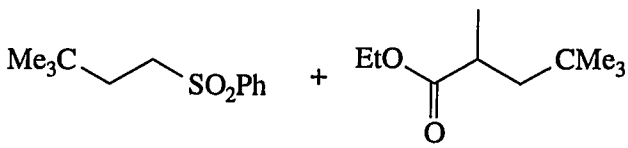


47% 10.3%

k_1/k_2
5.8

pp. Phenyl Vinyl Sulfone and Ethyl Methacrylate

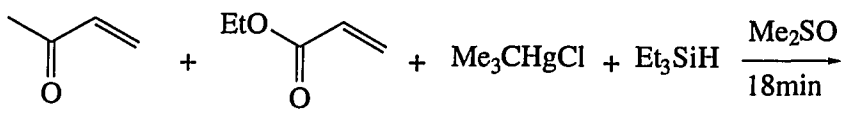


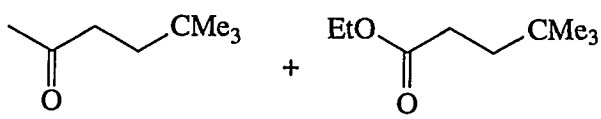


25.8% 17.1%

k_1/k_2
1.6

qq. Methyl Vinyl Ketone and Ethyl Acrylate

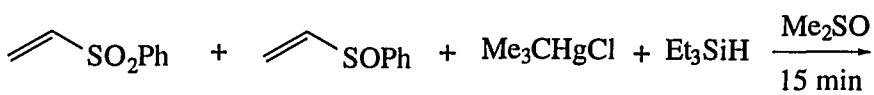


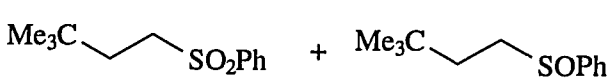


18.6% 17.4%

k_1/k_2
1.08

rr. Phenyl Vinyl Sulfone and Phenyl Vinyl Sulfoxide

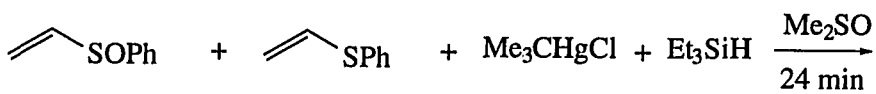


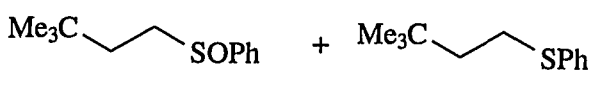


40% 4.0%

k_1/k_2
12.5

ss. Phenyl Vinyl Sulfoxide and Phenyl Vinyl Sulfide

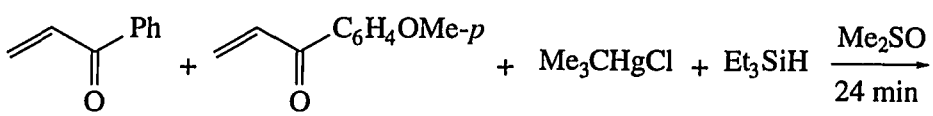


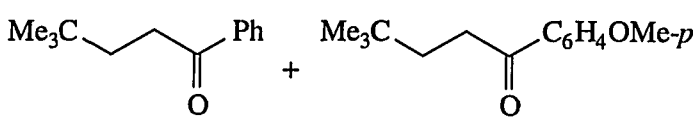


21.7% 8.5%

k_1/k_2
2.75

tt. Phenyl Vinyl Ketone and *p*-Methoxyphenyl Vinyl Ketone

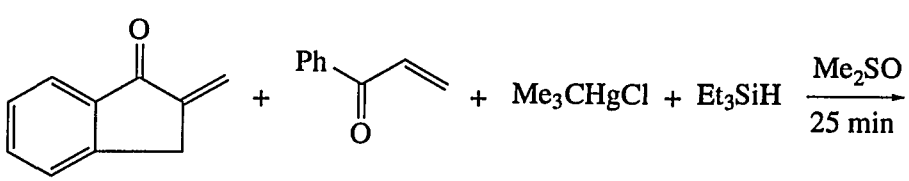


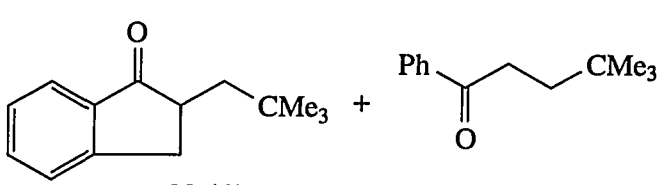


21% 14%

k_1/k_2
1.56

uu. 2-Methylene-1-indanone and Phenyl Vinyl Ketone

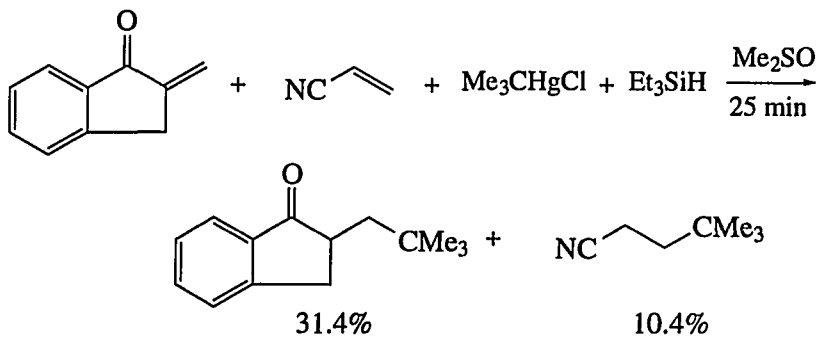




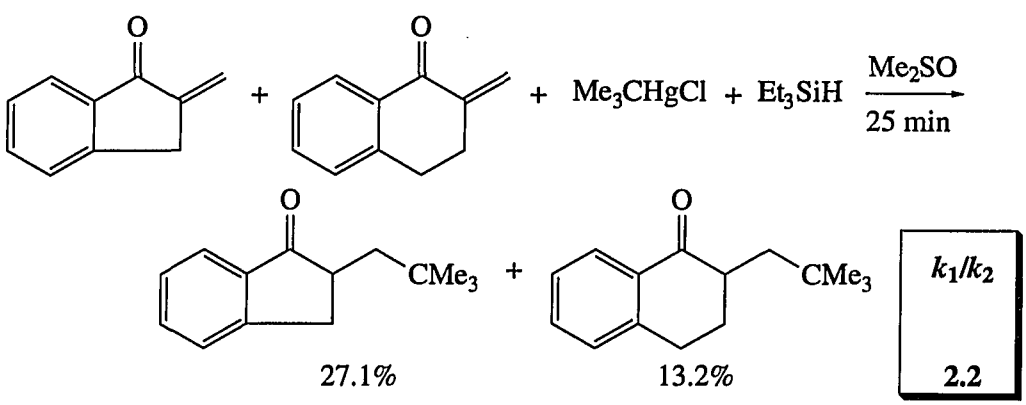
23.4% 14.8%

k_1/k_2
1.66

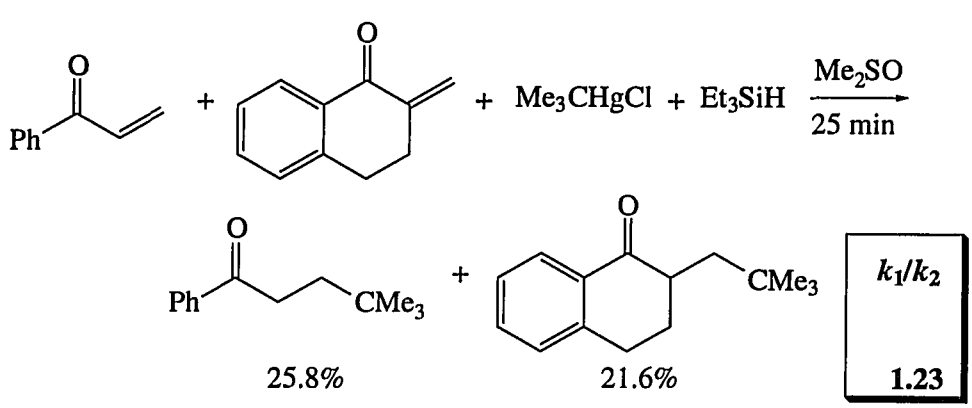
vv. 2-Methylene-1-indanone and Acrylonitrile



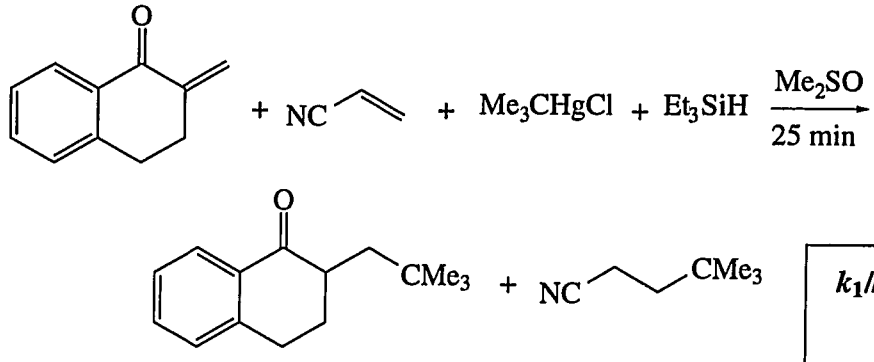
ww. 2-Methylene-1-indanone and 2-Methylene-1-tetralone



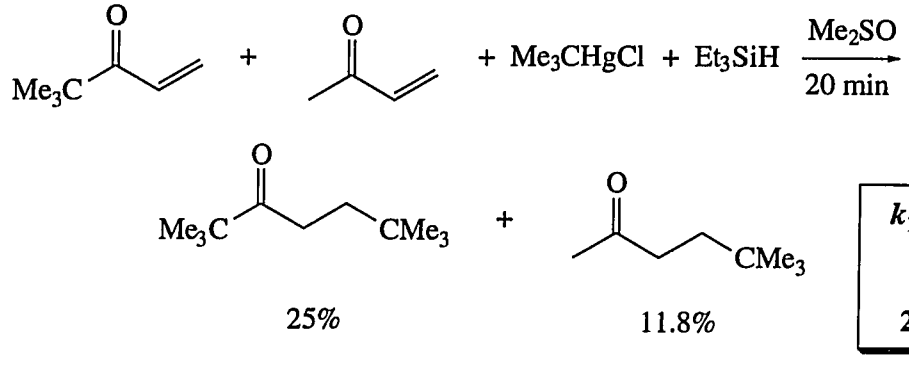
xx. Phenyl Vinyl Ketone and 2-Methylene-1-tetralone



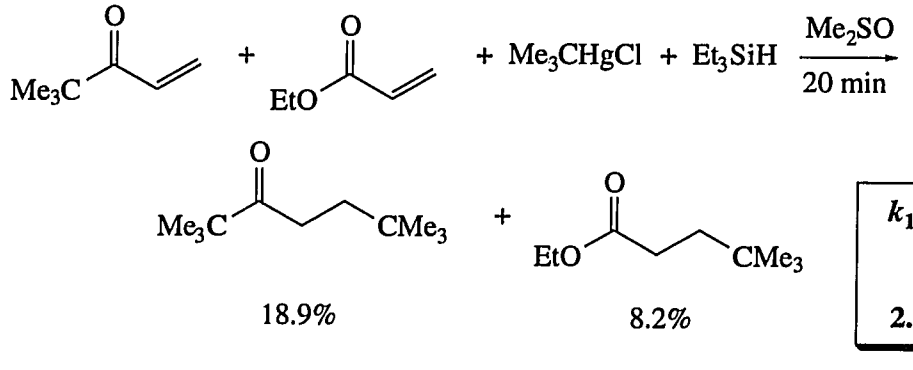
yy. 2-Methylene-1-tetralone and Acrylonitrile



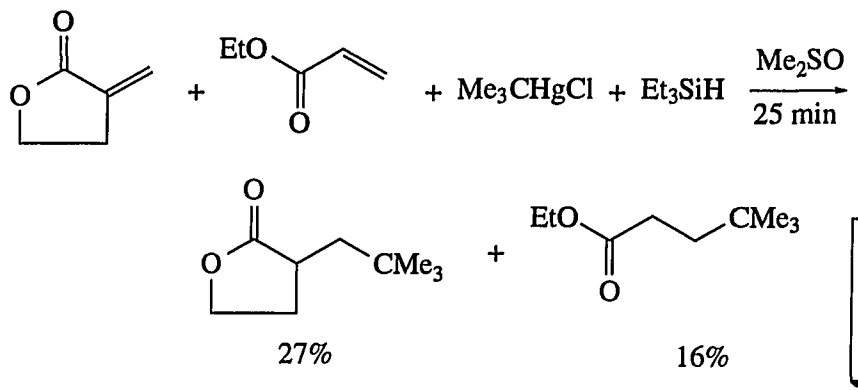
zz. 1,1-Dimethylethyl Vinyl Ketone and Methyl Vinyl Ketone



aaa. 1,1-Dimethylethyl Vinyl Ketone and Ethyl Acrylate



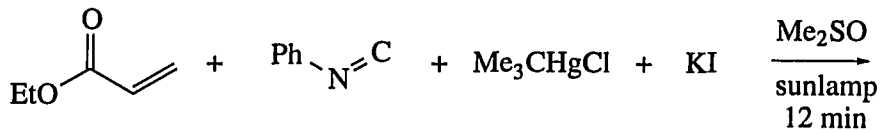
bbb. α-Methylene-γ-butyrolactone and Ethyl Acrylate

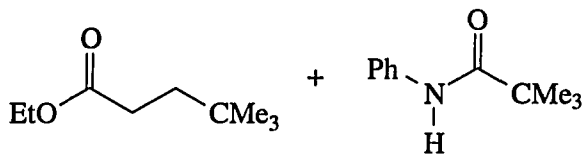


4. Relative Reactivities of Various Compounds toward *tert*-Butyl Radical Measured by Photostimulated Reactions

In cases where substrates did not work well with the silane system, photostimulated radical alkylation conditions were employed for the measurement of reactivities of these substrates. Competition reactions were conducted with excess amount of *tert*-butylmercury chloride and rate ratios were calculated using equation 34. Typically 0.1 mmol of each substrate, 0.4 mmol of *tert*-butylmercury chloride, and 0.8 mmol of KI (or NaI) were irradiated with 275 W fluorescent sunlamp at *ca.* 35 °C in 4 mL of Me_2SO. The ^1H NMR and GC yields were determined with toluene (0.1 mmol) as an added internal standard. Results are presented in following equations for the measurement of relative reactivities of each pair of substrates. The reaction of (E)-β-iodostyrene with *tert*-butylmercury chloride to yield (E)-(1,1-dimethylbutenyl)benzene was used where possible as a standard reaction with which to compare the reactivity of the various substituted alkenes.

a. Ethyl Acrylate and Phenylisocyanide

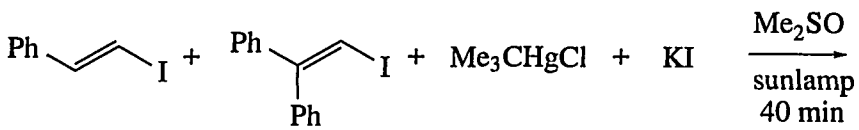


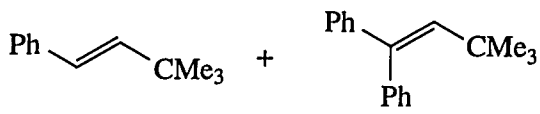


67% 63%

k_1/k_2
1.1

b. (E)-β-Iodostyrene and 2-Iodo-1,1-diphenylethylene[92]

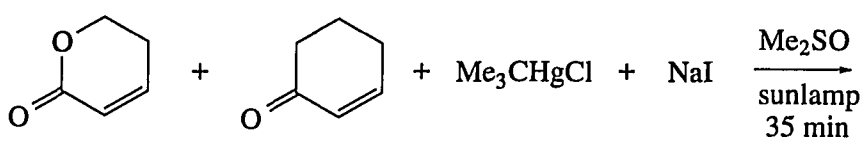


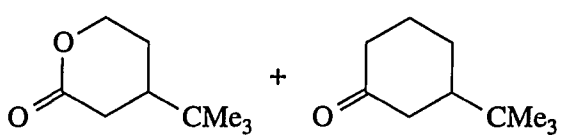


47.3% 20.1%

k_1/k_2
2.85

c. 5,6-Dihydro-(2*H*)-pyran-2-one and 2-Cyclohexenone

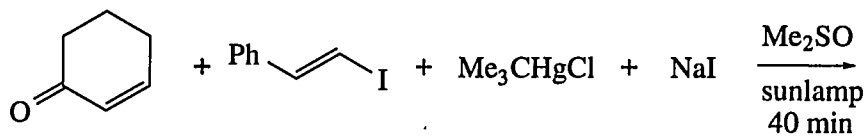


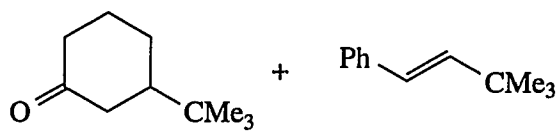


8.7% 7.9%

k_1/k_2
1.1

d. 2-Cyclohexenone and (E)-β-Iodostyrene

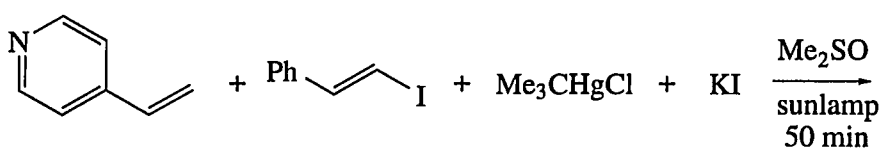


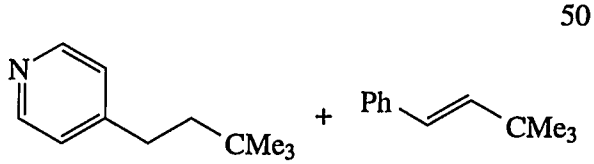


32.3% 25.3%

k_1/k_2
1.34

e. 4-Vinylpyridine[a] and (E)-β-Iodostyrene



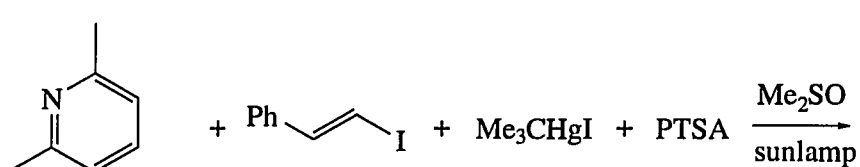


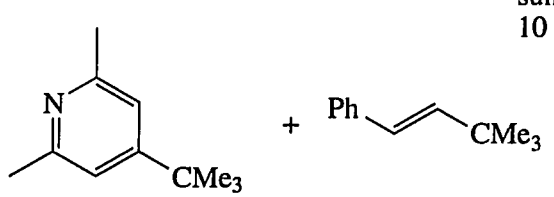
20.3% 2.3%

k_1/k_2
9.8

[a]The relative rate was measured averaged 550 for two runs in the persence of 4 equiv. of PTSA.

f. 2,6-Lutidine and (E)-β-Iodostyrene

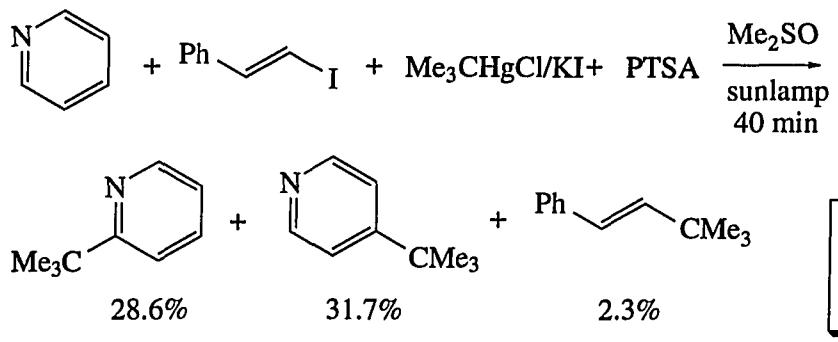




13% 15%

k_1/k_2
0.86

g. Pyridine and (E)-β-Iodostyrene



Competition reaction between pyridine and (E)-β-iodostyrene was conducted by using excess amount of substrates (0.5 mmol) with *tert*-butylmercury chloride (0.1 mmol) and KI (0.2 mmol) in the presence of PTSA (0.5 mmol) under the irradiation of 275 W fluorescent sunlamp at *ca.* 35 °C in Me_2SO (5 mL).

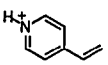
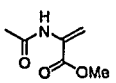
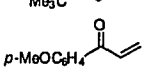
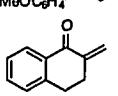
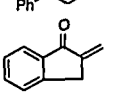
Since the value of $k_{add.}$ of *tert*-butyl radical to diethyl vinylphosphonate has been measured at 233 K as 5.9 x 10^4 $M^{-1}s^{-1}$, the absolute rate constant for addition of *tert*-butyl radical to (E) -β-iodostyrene can be estimated as 2.5 x 10^4 $M^{-1}s^{-1}$ based on the measured relative reactivities of CH_2=CHP(O)$(OEt)_2$: (E) -β-iodostyrene = 19.2 : 1.0[93,94] (using E_a = 4 kcal/mol).

D. Conclusion

The relative reactivities of a variety of substituted olefins and a few pyridines towards *tert*-butyl radical addition are summarized in Table XXVIII and converted to relative rates versus (E)-β-iodostyrene as the common standard.

Rate increase was observed with electron withdrawing groups at α-position of ethyl acrylate, acrylonitrile, and phenyl vinyl ketone.

Table XXVIII. Relative Reactivities[a] of Alkene toward *tert*-Butyl Radical

Entry	Alkene	k_{rel}	Entry	Alkene	k_{rel}
1		0.35	19		80
2		0.86[b]	20		100
3		1.0	21		60
4		9.8	22		90
5		550[b]	23		120
6		15[b]	24		162
7		1.3	25		230
8		1.5	26		330
9		1.6	27		1086
10		2.9	28		73
11		4.0	29		97
12		10	30		200
13		16	31		220
14		19	32		320
15		24	33		400
16		59	34		500
17		230	35		810
18		1080	36		840

[a] k_{rel} values are relative rates versus (E)-β-iodostyrene.
[b] Relative rate of protonated substrate for oxidative alkylation.

The reactivities of the three series are controlled mainly by polar effects with reactivity increasing from R = Me < H < Ph < Cl for the nucleophilic *tert*-butyl radical.[95] However, the relative reactivities of the ketones and esters show a puzzling variation with the nature of R. We believe this reflects mainly a variation in the preferred conformation of the α,β-unsaturated ketones where phenyl vinyl ketone is known to exist in the *s-cis* conformation (84%, entry 32 in Table XXVIII) but α-substituted derivatives prefer the *s-trans* structure.[96] Thus, 1,1-dimethylethyl vinyl ketone (100% of *s-cis*)[97] has a reactivity towards *tert*-butyl radical of 220 while methyl vinyl ketone (71% of *s-trans*)[97] has a reactivity of only 97. The reactivities of substrates in entries 22, 31, and 33 confirm the high reactivities of *s-cis* enones in radical additions. α-methylene-1-indanone is more reactive than α-methylene-1-tetralone probably because the former is coplanar and the latter is slightly twisted. The dramatic decrease in reactivity of phenyl 2-propenyl ketone compared to phenyl vinyl ketone reflects partially the inductive effect of the methyl group but mainly the switch in preferred conformation from *s-cis* to *s-trans*. Now ethyl methacrylate (*s-trans*, reactivity 60) is nearly as reactive as phenyl 2-propenyl ketone (*s-trans*, reactivity 73) or methyl vinyl ketone (71% *s-trans*, reactivity 97) and a similar effect is observed with α-phenyl or α-chloro derivatives.

E. Experimental Section

1. General Consideration

^{1}H NMR spectra were recorded at 300 MHz with a Nicolet NT300 spectrometer. Product yields were determined by integration of the ^{1}H NMR spectrum with a known amount of toluene as an internal standard and confirmed by gas chromatographic analysis performed on a Perkin-Elmer 3920 Gas Chromatograph with a packed chromosorb W (80-

100 mesh) column coated with 7% OV-3 and a hydrogen flame ionization detector. Product yields by GC analysis were determined by addition of a known amount of toluene as an internal standard by use of correction factors determined for the isolated compounds. *tert*-Butylmercury chloride was prepared as previously described (see chapter I). Most reagents were purchased from Aldrich chemical company and used without further purification. Solvents were purchased and dried as mentioned in chapter I.

2. Determination of Initial Kinetic Chain Length of *tert*-Butylation of Ethyl Methacrylate in the Presence of Triethylsilane

Ethyl methacrylate (0.2 mmol), *tert*-butylmercury chloride (0.4 mmol) were dissolved in 1.2 mL of nitrogen-purged Me_2SO-d_6. Toluene (0.2 mmol) was introduced into the solution as an internal standard. The solution was divided into two NMR tubes (0.6 mL in each tube) which were equipped with rubber septa. After a ^1H NMR spectrum of initial solution was obtained, triethylsilane (0.2 mmol) was syringed into the reaction mixture. The progress of the reaction was monitored at different reaction times by ^1H NMR integration. The reaction in the presence of 20 mol% of di-*tert*-butyl nitroxide was carried out under the same conditions. The yields of the product at different times are listed in Table XXV and the data are plotted in Figure II (page 87).

3. Determination of Initial Kinetic Chain Length of the Reaction between 3,3-Diacetylpropylmercuric Chloride and Diphenyl Disulfide

3,3-Diacetylpropylmercuric chloride (0.2 mmol) and PhSSPh (0.2 mmol) were dissolved in 2.0 mL of nitrogen-purged Me_2SO-d_6. Toluene (0.2 mmol) was introduced into the solution as an internal standard. The solution was divided into two NMR tubes

(1.0 mL in each tube) which were equipped with rubber septa. After a ^{1}H NMR spectrum of initial solution was obtained, the reaction mixture was irradiated with a 275 W GE sun lamp *ca.* 25 cm from the reaction tube. The progress of the reaction was monitored at different reaction times by ^{1}H NMR integration. The reaction in the presence of 10 mol% of di-*tert*-butyl nitroxide or potassium iodide (0.2 mmol) was carried out under the same conditions. The yields of the product at different time are listed in Table XXVI and the data are plotted in Figure III (page 90). Preparation of the 3,3-diacetylpropylmercuric chloride and its reaction product with PhSSPh are described in chapter III.

4. Preparation of (E)-β-Iodostyrene[98]

Phenylacetylene (50 mmol) and catecholborane (50 mmol) were stirred in a 100 mL flask for 2 hours under nitrogen at 70 °C to form the catechol ester of phenylethenylboric acid. The mixture was cooled to room temperature and stirred with 50 mL of water for 2 hours at room temperature, to effect the hydrolysis of the ester. The resulting mixture was cooled to 0 °C and the white solid, *trans*-phenylethenylboric acid, was collected by filtration and washed free of the catechol using ice-cold water. The boronic acid was then dissolved in 50 mL of ether in a 500 mL flask and cooled to 0 °C. Aqueous NaOH (50 mL, 3 N) was then added followed by 60 mmol of elemental iodine (20% excess) in 150 mL of ether, while stirring at 0 °C. The mixture was stirred for an additional 30 min at 0 °C. The excess iodine was distroyed with aqueous sodium thiosulfate solution. The ether solution was separated, washed with water, and dried over anhydrous $MgSO_4$. After removing the solvent, the pure β-iodostyrene was obtained in 56% yield by distillation; ^{1}H NMR ($CDCl_3$) δ 6.82 (d, 1H, *J*=15.0 Hz), 7.27-7.38 (m, 5H), 7.43 (d, 1H, *J*=15.0 Hz). The ^{1}H NMR spectrum agreed with literature values.[98]

5. Preparation of 2-Iodo-1,1-diphenylethylene

2-Iodo-1,1-diphenylethylene was prepared by the literature method.[92] This compound was identified by ^{1}H NMR and confirmed by comparison of the spectral data with the literature; ^{1}H NMR ($CDCl_3$) δ 6.926 (s, 1H), 7.18-7.30 (m, 6H), 7.34-7.45 (m, 4H).

6. General Procedure for the Competition Reactions with Et_3SiH

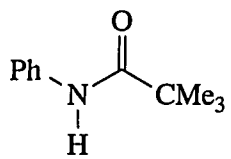
The two substrates (0.1 mmol each) and *tert*-butylmercury chloride (0.4 mmol) were dissolved in 4 mL of deoxygenated Me_2SO in a Pyrex test tube equipped with a rubber septum. Triethylsilane (0.4 mmol) was syringed into the reaction tube. The reaction mixture was stirred in the dark and quenched with aqueous sodium thiosulfate solution before the reaction was complete. The reaction mixture was extracted three times with 15 mL of methylene chloride. The combined methylene chloride extract was washed with aqueous sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The GC and ^{1}H NMR yields were determined with added toluene (0.1 mmol) as an internal standard. Preparation of substrates and their *tertt*-butylation products are described in Chapter I.

7. General Procedure for Competition Reactions under Irradiation

The two substrates (0.1 mmol each) and *tert*-butylmercury chloride (0.4 mmol) were dissolved in 4 mL of deoxygenated Me_2SO in a Pyrex test tube equipped with a rubber septum. The reaction mixture was stirred with irradiation from a 275 W fluorescent sunlamp at *ca.* 35 °C for a period of time and quenched with aqueous sodium thiosulfate

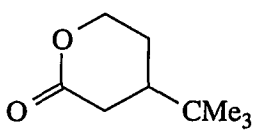
solution before the reaction was complete. The reaction mixture was extracted three times with 15 mL of methylene chloride. The combined methylene chloride extracts were washed with aqueous sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The GC and ^1H NMR yields were determined with added toluene (0.1 mmol) as an internal standard. Following compounds were isolated.

a. 2,2-dimethyl-*N*-Phenylpropanamide[99]



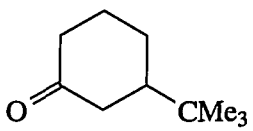
This compound was isolated as a white solid, mp 128-130 °C; ^1H NMR ($CDCl_3$) δ 1.316 (s, 9H), 4.104 (s, 1H), 7.092 (t, 1H, *J*=7.2 Hz), 7.312 (t, 2H, *J*=7.5 Hz), 7.522 (d, 2H, *J*=8.4 Hz).

b. 4-(1,1-Dimethylethyl)tetrahydro-2*H*-pyran-2-one[100]



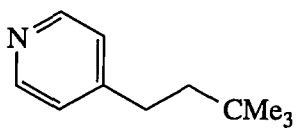
The compound was isolated and identified by comparison of its ^1H NMR spectral data with the literature;[72] ^1H NMR ($CDCl_3$) δ 0.896 (s, 9H), 1.42-1.85 (m, 3H), 2.10-2.25 (m, 1H), 2.45 (m, 1H), 4.08-4.18 (m, 1H), 4.25-4.34 (m, 1H).

c. 3-(1,1-Dimethylethyl)cyclohexanone[100]



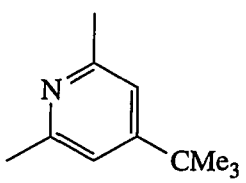
The compound was isolated and identified by comparison of its ^{1}H NMR spectral data with the literature;[72] ^{1}H NMR ($CDCl_3$) δ 0.889 (s, 9H), 1.31-1.82 (m, 5H), 2.10-2.40 (m, 4H).

d. 4-(3,3-Dimethylbutyl)pyridine[20]



This compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.966 (s, 9H), 1.46-1.53 (m, 2H), 2.53-2.59 (m, 2H), 7.110 (d, 2H, *J*=5.4 Hz), 8.469 (d, 2H, *J*=5.7 Hz); GCMS *m/z* (rel intensity) 163 ($M^{+\cdot}$, 31), 148 (25), 118 (4), 107 (61), 93 (12), 92 (16), 65 (18), 57 (100); HRMS calcd for $C_{11}H_{17}N$ 163.1361, found 163.1362.

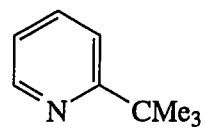
e. 4-(1,1-Dimethylethyl)-2,6-dimethylpyridine[101]



The compound was isolated as a yellow solid, mp 56-58 °C; ^{1}H NMR ($CDCl_3$) δ 1.288 (s, 9H), 2.521 (s, 6H), 6.949 (s, 2H); GCMS *m/z* (rel intensity) 163 ($M^{+\cdot}$, 34), 148

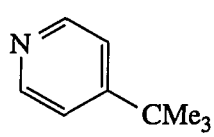
(100), 120 (18), 91 (9), 77 (8), 57 (2); HRMS calcd for $C_{11}H_{17}N$ 163.1361, found 163.1363.

f. 2-(1,1-Dimethylethyl)pyridine[20]



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.372 (s, 9H), 7.078 (ddd, 1H, *J*=0.6, 4.8, 7.2 Hz), 7.335 (d, 1H, *J*=7.8 Hz), 7.602 (dt, 1H, *J*=1.8, 7.8 Hz), 8.562 (d, 1H, *J*=4.8 Hz); ^{13}C NMR ($CDCl_3$) δ 30.184 (q), 37.366 (s), 119.059 (d), 120.580 (d), 136.110 (d), 148.501 (d), 169.207 (s); GCMS *m/z* (rel intensity) 135 ($M^{+\cdot}$, 25), 134 (29), 120 (100), 104 (6), 93 (33), 79 (21), 51 (15); HRMS *m/z* calcd for $C_9H_{12}N$ (M^+-1) 134.0970, found 134.0985.

g. 4-(1,1-Dimethylethyl)pyridine[20]

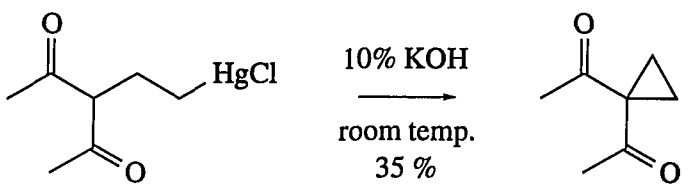


The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.315 (s, 9H), 7.275 (dd, 2H, *J*=1.5, 4.5 Hz), 8.506 (dd, 2H, *J*=1.5, 4.8 Hz); ^{13}C NMR ($CDCl_3$) δ 30.475 (q), 34.616 (s), 120.677 (d), 149.504 (d), 159.922 (s); GCMS *m/z* (rel intensity) 135 ($M^{+\cdot}$, 43), 120 (100), 104 (3.6), 92 (46), 51 (17); HRMS *m/z* calcd for $C_9H_{13}N$ 135.1048, found 135.1052.

CHAPTER III. REACTIONS OF 3, 3-DIACETYLPROPYLMERCURIC CHLORIDE

A. Introduction

Usually organomercurials are quite stable towards base. However, when 3,3-diacetylpropylmercuric chloride was treated with 10% aqueous potassium hydroxide at room temperature, instantaneous formation of metallic mercury was observed, and 1,1-diacetylcyclopropane was obtained as the only detectable organic product with 35% yield.[102]



71 72 (33)

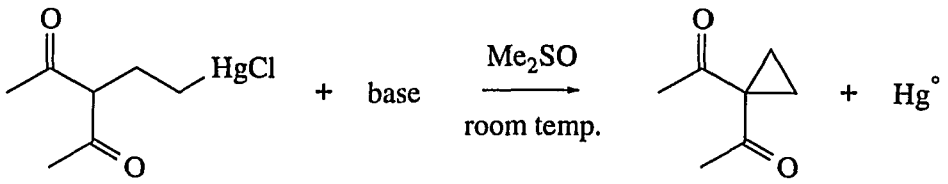
In order to account for this unusual reactivity and to explore the possible radical reactions with this material a series of studies have been carried out for the reactions of 3,3-diacetylpropylmercuric chloride.

B. Results and Discussion

1. Reactions of 3,3-Diacetylpropylmercuric Chloride with Base

Reactions of 3,3-diacetylpropylmercuric chloride with different bases were carried out at room temperature. Results are summarized in Table XXIX.

Table XXIX. Reactions of 3,3-Diacetylpropylmercuric Chloride with Base in Me_2SO[a]



71 **72**

Entry	Base	Reaction Time	Yield[b] of **72**, %
1	$KOCMe_3$	30 min	61
2	NaOPh	40 min	50
3	$NaOCH_3$	2 h	58
4	DABCO	24 h	No Reaction
5	Pyridine	24 h	No Reaction
6	Li_2CO_3	24 h	No Reaction

[a]Reaction of 0.25 mmol of 3,3-diacetylpropylmercuric chloride and a base in 5 mL of Me_2SO.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

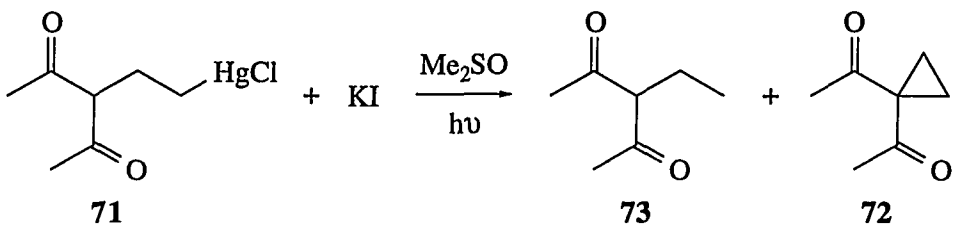
Demercuration of this mercurial with base not only occurs in aqueous solution, but also takes place in dimethyl sulfoxide with strong base. A better yield of the cyclized product was obtained with a stronger base. Reaction does not occur with weak bases in 24 hours, indicating that probably a deprotonation reaction is involved.

2. Reactions of 3,3-Diacetylpropylmercuric Chloride under Irradiation

In order to find out whether the radical is involved, 3,3-diacetylpropylmercuric chloride was tested under conditions known to promote radical formation. The compound was irradiated in a Rayonet photochemical reactor (350 nm) or under a 275 W fluorescent sunlamp. No reaction was observed in 18 hours. When 4 equiv. of KI was introduced to

form the more reactive mercuric iodide, a mixture of 1,1-diacetylcyclopropane (**72**) and an acyclic product, 3-ethyl-2,4-pentadione (**73**), was obtained due to the hydrogen abstration of the radical from the starting material followed by an internal homolytic substiuttion (S_{Hi}) process (Scheme XIII on page 128).

Table XXX. Reactions of **71** in the Presence of KI[a]



71 **73** **72**

Entry	Molar Equivalent KI	Molar Equivalent $K_2S_2O_8$	Time (h)	Yield, %[b] **73**	Yield, %[b] **72**
1	4		S. L. 24	22	26
2	4		Dark 24		5
3	4	2	S. L. 24	19	10

[a]Reaction of 0.25 mmol of **71** with 4 equiv. of KI in 5 mL of Me_2SO with 275 W fluorescent sunlamp irradiation at *ca.* 35 °C.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.

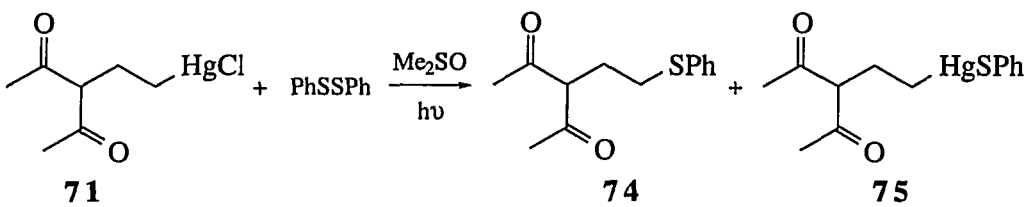
3. Reactions of 3,3-Diacetylpropylmercuric Chloride with Radical Trapping Reagents

Radical trapping reagents were used to trap any radical intermediate. When lithium nitronate ($LiO_2N{=}CMe_2$) was used, no trapped product was ever obtained, even under sunlamp irradiation. Instead, 47% of 1,1-diacetylcyclopropane was the only detected product. Apparently the nitronate acted as a base and the ionic reaction overrode the slow radical reaction. When diphenyl disulfide, a good radical trapping reagent, was added to a

dimethyl sulfoxide solution of 3,3-diacetylpropyl mercuric chloride, no reaction was observed in the dark. However, when this solution was irradiated under sunlamp 3,3-diacetylpropyl phenyl sulfide was obtained as the major product. A small amount of 3,3-diacetylpropyl-mercuric phenyl sulfide was also observed.

Interestingly, the reaction with PhSSPh in the dark in the presence of a base, potassium *tert*-butoxide, gave the 3,3-diacetylpropylmercuric phenyl sulfide and a mixed disulfide product **76**. The demercuration reaction with base was completely inhibited by the presence of PhSSPh (reaction 35). A sequential reaction was conducted in order to study the sequence of the product formation (Scheme XI).

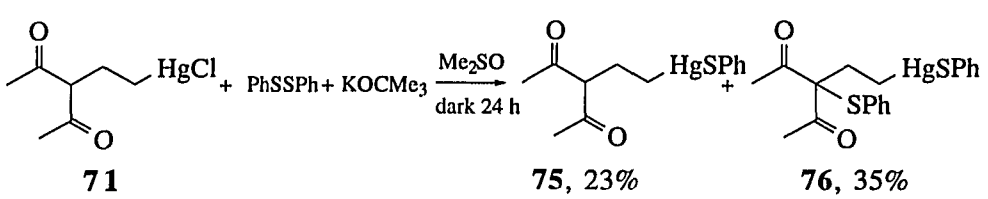
Table XXXI. Reaction of **71** with PhSSPh[a]



71 **74** **75**

Entry	71	Molar Equivalent PhSSPh (time, h)	Yield, %[b] 74	75
1	1	1.0 (12)	70	5
2	1	0.5 (36)	30	25
3	1	1.0 (36), 0.5 (24)	66	5

[a]Reaction of 0.25 mmol of **71** with PhSSPh in 5 mL of Me_2SO with 275 W fluorescent sunlamp irradiation at *ca.* 35 °C.
[b]By GC and ^1H NMR integration with toluene (0.1 mmol) as an added internal standard.



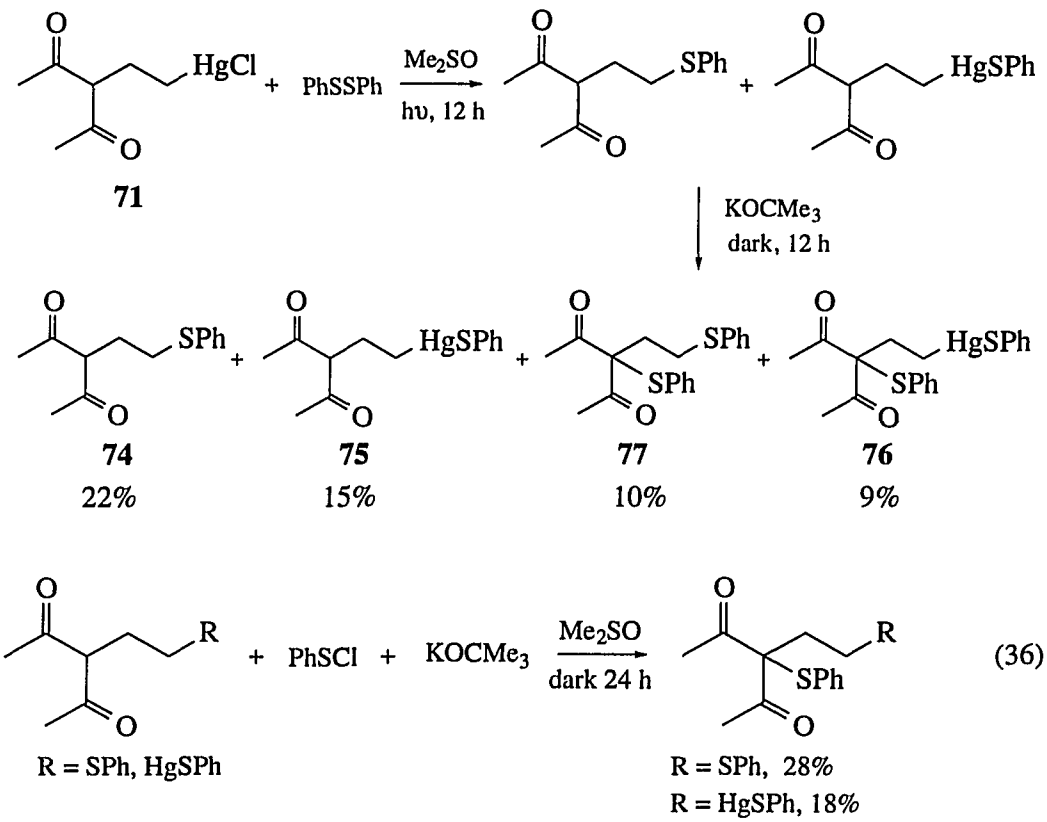
71 **75**, 23% **76**, 35% (35)

The reaction of 3,3-diacetylpropylmercuric phenyl sulfide **75** with PhSSPh and base in the dark gave only 5% of product **76**, indicating that the formation of disulfide **76** by phenylthiolation of **75** is not the major reaction pathway.

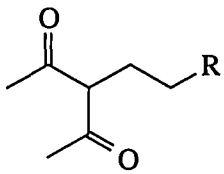
Results for the reaction of **74** or **75** with PhSCl (reaction 36) suggested that the substitution of the methine hydrogen by PhS could be an ionic process.

However, substitution by PhSSPh did not occur without the presence of the mercuric chloride (reaction 37).

Scheme XI. Reaction with PhSSPh Followed by Addition of $KOCMe_3$



(36)



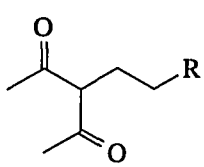
R = SPh, H

+ PhSSPh + $KOCMe_3$ $\xrightarrow[\text{dark 24 h}]{Me_2SO}$ No Reaction (37)

4. Kinetic Studies

The kinetic study for the demercuration of 3,3-diacetylpropylmercuric chloride with $KOCMe_3$ indicated that a radical process is not involved, since neither irradiation nor the addition of a radical scavenger altered the kinetic behavior of the reaction (Table XXXII and Fig. IV).

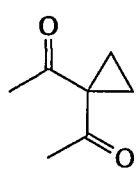
Table XXXII. Demercuration of **71** with $KOCMe_3$ Followed by ^1H NMR



71

+ $KOCMe_3$ $\xrightarrow{Me_2SO}$

1. Dark
2. Dark with 10% of $(Me_3C)_2NO^{\bullet}$
3. Sunlamp



72

Entry	Time (min)	Yield of Product **72**, % in the dark	with DTBN	sunlamp
1	4	25.4	28.0	
2	6			32.0
3	8	31.8	32.3	
4	12	36.0		39.3
5	20	40.7	44.6	
6	24	42.4		
7	26		45.1	48.9
8	28	44.1		
9	32		47.0	50.0

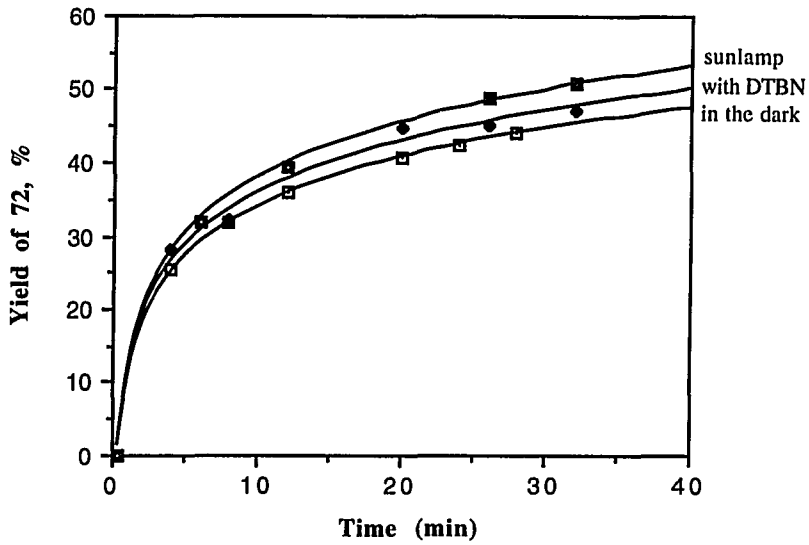


Figure IV. Yield of Product **72** Plotted against Reaction Time

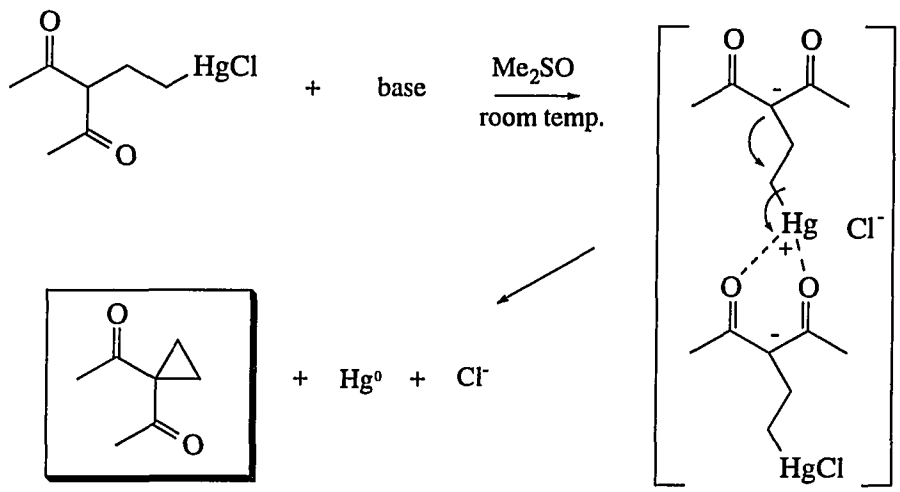
In the reaction of **71** with PhSSPh under irradiation, kinetic behavior consistent with a radical chain is discovered. Upon addition of 10 mol% of di-*tert*-butyl nitroxide which is known as a radical scavenger, the reaction is inhibited. The kinetic chain length has been measured as 32 (page 88).

C. Mechanistic Consideration

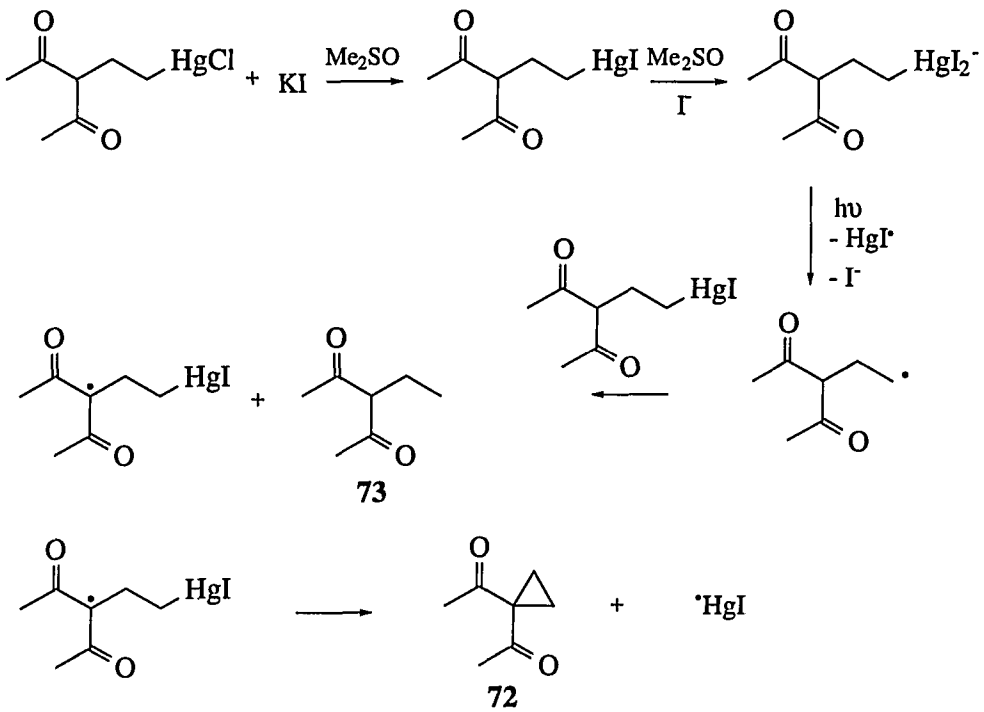
1. Demercuration of 3,3-Diacetylpropylmercuric Chloride with Base

Demercuration with base is an ionic process in which the anionic carbon generated by deprotonation attacks the carbon adjacent to mercury. This process is made possible by carbonyl chelation of Hg which weakens the C-Hg bond (Scheme XII).

Scheme XII. Mechanism for Demercuration with Base



Scheme XIII. Mechanism of Reaction of **71** with KI



2. Reaction of 3,3-Diacetylpropylmercuric Chloride in the Presence of KI

The reaction of 3,3-diacetylmercuric chloride with KI gives the mercurate complex followed by radical formation upon irradiation. One route to the approximately equal amount of 1,1-diacetylcyclopropane (**72**) and 3-ethyl-2,4-pentadione (**73**) involves the reactions shown in Scheme XIII.

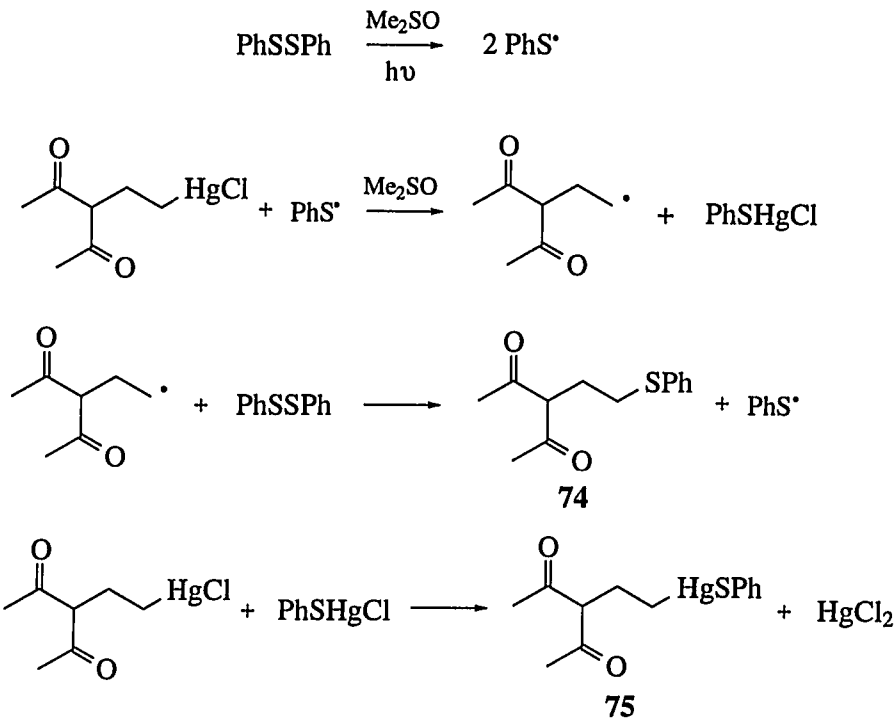
3. The reaction of 3,3-Diacetylpropylmercuric Chloride with PhSSPh under Irradiation

In the reaction of **71** with PhSSPh under irradiation, the phenylthiyl radical is formed by photolysis, followed by displacement of the diacetylpropyl radical. This radical then attacks diphenyl disulfide to give the diacetylpropyl phenyl sulfide (**74**) and the phenylthiyl radical which propagates the chain. The diacetylpropylmercuric phenyl sulfide could be obtained by standard redistribution reactions (Scheme XIV).

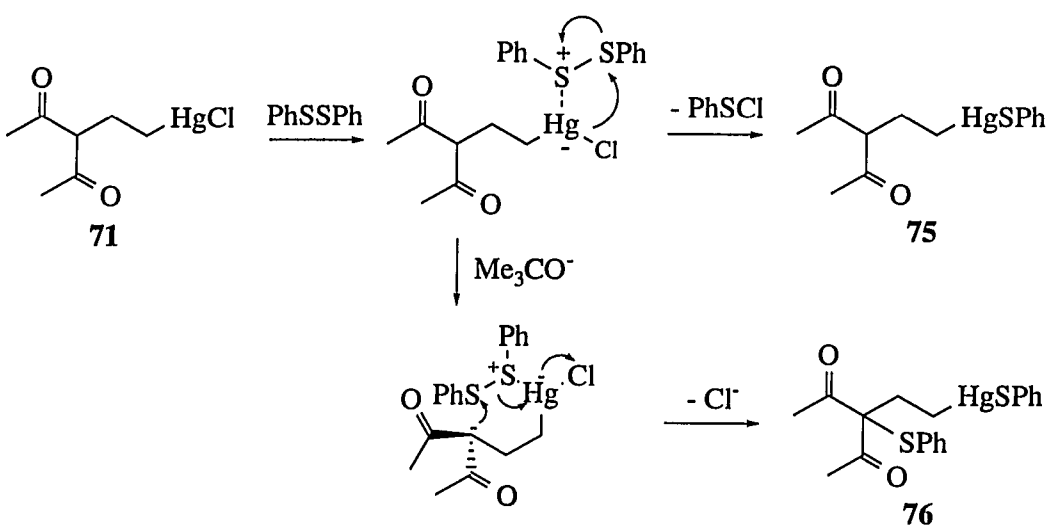
4. The reaction of 3,3-Diacetylpropylmercuric Chloride with PhSSPh and Base in the Dark

In the reaction of **71** with PhSSPh and base in the dark, sulfur with its greater affinity for mercury than oxygen, completely prevents the chelation of carbonyl groups. The complex between **71** and PhSSPh can either lose PhSCl to form 3,3-diacetylpropylmercuric phenyl sulfide (**75**) or in the presence of $KOCMe_3$ form the enolate anion which can react to form 3,3-diacetyl-3-phenylthiopropylmercuric phenyl sulfide (**76**) (Scheme XV). As shown in Scheme XI, the conversion of **75** to **76** does not seem to be an important process.

Scheme XIV. Mechanism of Reaction of **71** with PhSSPh under Irradiation



Scheme XV. Mechanism of Reaction of **71** with PhSSPh and Base in the Dark



D. Conclusion

The demercuration of 3,3-diacetylpropylmercuric chloride with strong bases to form 1,1-diacetylcyclopropane not only occurs in aqueous solution but in organic solvents as well. Experimental results suggest that the reaction involves an intramolecular nucleophilic displacement of mercury from the attack of the enolate carbon atom. The unusual reactivity of this substance is made possible by an intermolecular carbonyl chelation of the mercury. This demercuration reaction is completely inhibited by the presence of diphenyl disulfide since sulfur has greater affinity for mercury than oxygen. 3,3-Diacetylpropylmercuric chloride is also capable of undergoing radical reactions under irradiation.

E. Experimental Section

1. General Consideration

Analytical gas chromatography (GC) was performed on a Perkin-Elmer 3920 gas chromatograph equipped with a Hitachi D-2500 Chromato-integrator. ^{1}H and ^{13}C NMR spectra were obtained with a Nicolet NT300 spectrometer. Chemical shifts are reported in ppm from internal tetramethylsilane for ^{1}H NMR or for ^{13}C NMR measured relative to the central line of internal $CDCl_3$ at 77.000 ppm. GCMS were recorded on a Finnegan 4000 spectrometer with Incos data system and high resolution mass spectra were recorded on a Kratos MS-50 spectrometer. Infrared spectra (IR) were recorded on an IBM IR-98 FT spectrometer or Digital FTS-7 FT spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Most products were isolated by either flash column chromatography on silica gel (Kiesel gel, 230-400 mesh ATSM, purchased from EM Regents Co.) with mixed solvents as eluents or by preparative GC. GC yields were determined by using an internal standard (toluene) and were corrected with predetermined response factors. ^{1}H NMR spectroscopy yields were determined by integration with a known amount of an internal standard (toluene).

2. Solvents and Reagents

Solvents were purchased from Fisher and Baker. Dimethyl sulfoxide (Me_2SO) was distilled from calcium hydride and stored over 4Å Molecular Sieves under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium metal and benzene was distilled from calcium hydride. Other solvents were purchased and used without further purification.

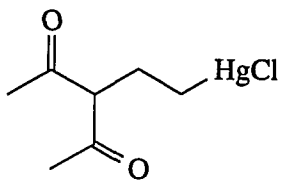
Chemical reagents in high purity grades were purchased mostly from Aldrich. In most cases, the reagents were used without further purification.

3. Preparation of 3,3-Diacetylpropylmercuric Chloride[102]

Into a mixture of mercury acetate (6.0 g., 20 mmol) and acetic acid (6.0 g.), ethylene was introduced with stirring until the mixture became clear and no formation of a yellow precipitate of mercuric oxide was observed upon adding the sample to 10% aqueous NaOH solution. Into this solution, acetylacetone (4.0 g., 40 mmol) and then 70% perchloric acid (1.5 g) were added at room temperature. After standing overnight, 10% aqueous NaCl solution was added. The resulting white crystals were separated and

recrystallized from ethanol to give the mercurial **71**, mp 132-133 °C (lit[102], 132-132.5 °C), 6.3 g in 85% yield.

a. 3,3-Diacetylpropylmercuric Chloride[102] (71)



This mercurial was purified as a white solid, mp 132-133°C; ^{1}H NMR ($CDCl_3$) δ 2.053 (t, 2H, *J*=8.1 Hz), 2.187 (s, 6H), 2.666 (t, 2H, *J*=8.1 Hz); GCMS *m/z* (rel intensity) 364 ($M^{+\cdot}$, 2), 336 (14), 321 (6), 127 (100), 111 (12), 99 (31), 85 (37), 69 (39), 67 (17), 55 (13).

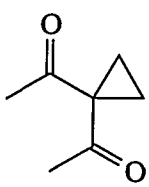
4. Demercuration of 3,3-Diacetylpropylmercuric Chloride with Base in Me_2SO

3,3-Diacetylpropylmercuric chloride (0.25 mmol) was dissolved in 5 mL of Me_2SO followed by addition of a Me_2SO solution of a base (0.25 mmol) at room temperature. An exothermic reaction occurred and metallic mercury was formed. After standing for 1 h, mercury was separated from the reaction solution by decantation. The reaction mixture was then extracted with ether three times. The combined ether extract was then washed with half-saturated aqueous sodium thiosulfate solution and water, and then dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and ^{1}H NMR. The yield of the product was measured by ^{1}H NMR integration with toluene as an added internal standard.

5. Procedure for the Photostimulated Reaction of 3,3-Diacetylpropylmercuric Chloride

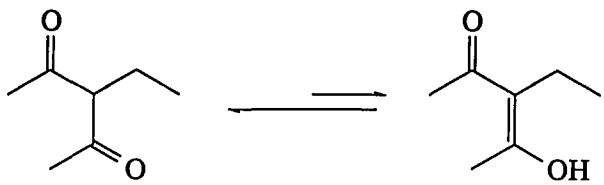
3,3-Diacetylpropylmercuric chloride (0.25 mmol) and KI (0.5 mmol) with or without $K_2S_2O_8$ were dissolved in a distilled and predeoxygenated Me_2SO (5 mL) in a Pyrex test tube equipped with a rubber septum. With stirring the solution was irradiated with a 275 W sunlamp *ca.* 25 cm from the reaction test tube for 12 hours. The reaction mixture was then poured in 15 mL of saturated aqueous sodium thiosulfate solution and extracted three times with ether (15 mL). The combined ether extract was washed with half-saturated aqueous sodium thiosulfate solution and water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and ^1H NMR and each product was isolated by flash column chromatography (1% of ethyl acetate in hexane) and characterized by instrumental analysis. Yields were determined by ^1H NMR with toluene (0.1 mmol) as an added internal standard.

a. 1,1-Diacetylcyclopropane[102] (72)



The compound was isolated as a liquid, bp 74 °C; ^1H NMR ($CDCl_3$) δ 1.475 (s, 4H), 2.228 (s, 6H); GCMS *m/z* (rel intensity) 126 ($M^{+\cdot}$, 7), 111 (23), 84 (5), 69 (36), 43 (100), 41 (11); HRMS calcd for $C_7H_{10}O_2$ 126.0681, found 126.0680.

b. 3-Ethyl-2,4-pentadione[103] (73)



73a **73b**

The compound was isolated as a liquid. In a solution such as in $CDCl_3$ there is a equilibrium between the keto and enol forms. The ratio of **73a** to **73b** in deuterated chloroform is estimated as 3 to 1 from ^1H NMR integration. ^1H NMR of **73a** ($CDCl_3$) δ 0.905 (t, 3H, *J*=7.5 Hz), 1.885 (m, 2H), 2.175 (s, 6H), 3.540 (t, 1H, *J*=7.2 Hz); ^1H NMR of **72b** ($CDCl_3$) δ 1.047 (t, 3H, *J*=7.5 Hz), 2.257 (q, 2H, *J*=7.5 Hz), 2.139 (s, 6H); GCMS *m/z* (rel intensity) 128 ($M^{+\cdot}$ 2), 113 (2), 100 (7), 86 (30), 85 (5), 71 (59), 58 (5), 55 (2), 44 (3), 43 (100), 41 (5).

6. Procedure for Photostimulated Reaction of 3,3-Diacetylpropylmercuric Chloride with Diphenyl Disulfide

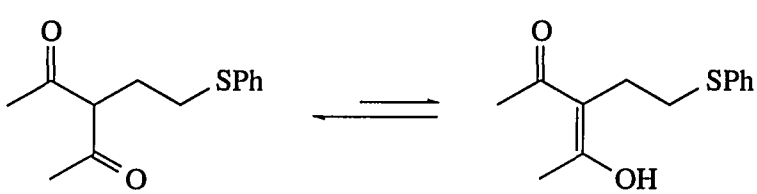
3,3-Diacetylpropylmercuric chloride (0.50 mmol) and PhSSPh (0.25-0.50 mmol) were dissolved in a distilled and predeoxygenated Me_2SO (5 mL) in a Pyrex test tube equipped with a rubber septum. With stirring the solution was irradiated with a 275 W sunlamp *ca.* 25 cm from the reaction test tube for a period of time (see results in section 2 of this chapter). The reaction mixture was then poured in 15 mL of water and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and ^1H NMR and each product was isolated by flash column chromatography (1% of ethyl acetate in hexane) and characterized by instrumental analysis.

Yields were determined by ^1H NMR with toluene (0.1 mmol) as an added internal standard.

7. Procedure for Reactions of 3,3-Diacetylpropylmercuric Chloride with Diphenyl Disulfide and $KOCMe_3$

3,3-Diacetylpropylmercuric chloride (0.50 mmol) and PhSSPh (0.50 mmol) were dissolved in a distilled and predeoxygenated Me_2SO (5 mL) in a Pyrex test tube equipped with a rubber septum. With stirring a solution of $KOCMe_3$ (0.50 mmol) was syringed into the reaction mixture, with or without a sunlamp irradiation (see results in section 2 of this chapter). The reaction mixture was then poured into 15 mL of water and extracted three times with methylene chloride (15 mL). The combined organic extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and ^1H NMR and each product was isolated by flash column chromatography (1% of ethyl acetate in hexane) and characterized by instrumental analysis. Yields were determined by ^1H NMR with toluene (0.1 mmol) as an added internal standard.

a. 3,3-Diacetylpropyl Phenyl Sulfide (74)

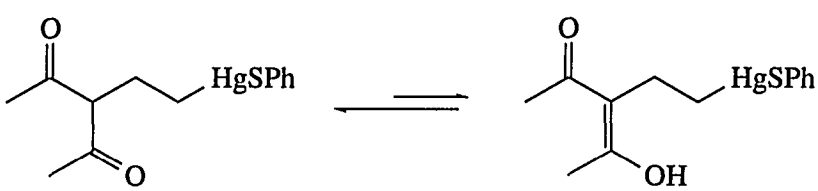


74a **74b**

The compound was isolated as a liquid. In a solution such as in $CDCl_3$ there is a equilibrium between the keto and enol forms. The ratio of **74a** to **74b** in deuterated

chloroform is estimated as 2 to 1 from ^{1}H NMR integration. ^{1}H NMR of **74a** ($CDCl_3$) δ 2.06-2.17 (m, 2H), 2.145 (s, 6H), 2.883 (t, 2H, *J*=7.2 Hz), 3.917 (t, 1H, *J*=6.9 Hz), 7.16-7.40 (m, 5H); ^{1}H NMR of **74b** ($CDCl_3$) δ 2.059 (s, 6H), 2.522 (t, 2H, *J*=8.1 Hz), 2.906 (t, 2H, *J*=9.0 Hz), 7.16-7.40 (m, 5H); ^{13}C NMR of **74a** ($CDCl_3$) δ 27.16 (t), 29.31 (q), 31.58 (t), 66.46 (d), 126.38 (d), 128.98 (d), 129.54 (d), 135.14 (s), 203.48 (s); ^{13}C NMR of **74b** ($CDCl_3$) δ 22.85 (q), 27.80 (t), 34.25 (t), 108.69 (d), 126.53 (d), 128.92 (d), 130.06 (d), 135.55 (s), 191.28 (s); GCMS *m/z* (rel intensity) 236 ($M^{+\cdot}$, 5), 137 (7), 136 (62), 135 (23), 127 (12), 123 (7), 113 (15), 91 (5), 85 (17), 45 (15), 43 (100); FTIR (neat) 3408 (w), 3061 (w), 2922 (m), 1724 (m), 1699 (s), 1358 (m) cm^{-1}; HRMS calcd for $C_{13}H_{16}O_2S$ 236.0871, found 236.0875; Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.06; H, 6.82; S, 13.58. Found: C, 65.91; H, 6.78; S, 14.44.

b. 3,3-Diacetylpropylmercuric Phenyl Sulfide (75)

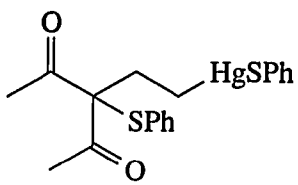


75a **75b**

The compound was isolated as a solid. In a solution such as in $CDCl_3$ there is a equilibrium between the keto and enol forms. The ratio of **75a** to **75b** in deuterated chloroform is estimated as 3 to 1 from ^{1}H NMR integration. ^{1}H NMR of **75a** ($CDCl_3$) δ 1.552 (t, 2H, *J*=8.4 Hz), 2.130 (s, 6H), 2.28 (m, 2H), 3.558 (t, 1H, *J*=6.9 Hz), 7.15-7.23 (m, 3H), 7.36-7.42 (m, 2H); ^{1}H NMR of **75b** ($CDCl_3$) δ 1.806 (t, 2H, *J*=8.1 Hz), 2.101 (s, 6H), 2.632 (t, 2H, *J*=8.1 Hz), 7.07-7.14 (m, 5H), 7.36-7.42 (m, 2H); ^{13}C NMR of **75a** ($CDCl_3$) δ 27.17 (t), 29.29 (q), 32.93 (t), 72.16 (d), 125.32 (d), 128.75 (d), 132.98 (d), 135.32 (s), 204.00 (s); ^{13}C NMR of **75b** ($CDCl_3$) δ 22.87 (q), 26.56 (t),

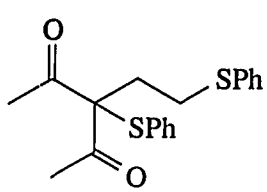
36.16 (t), 113.38 (d), 125.32 (d), 128.75 (d), 132.98 (d), 135.32 (s), 190.80 (s); GCMS *m/z* (rel intensity) 438 ($M^{+\cdot}$ 0.4), 420 (2), 218 (9), 185 (3), 154 (5), 127 (26), 110 (27), 109 (88), 85 (21), 77 (7), 69 (15), 65 (38), 51 (9), 43 (100), 39 (29); HRMS calcd for $C_{13}H_{16}O_2SHg$ 438.0577, found 438.0589.

c. 3,3-Diacetyl-3-phenylthiopropylmercuric Phenyl Sulfide (76)



The compound was isolated as a solid, mp 101-102 °C; ^{1}H NMR ($CDCl_3$) δ 1.387 (t, 2H, *J*=7.2 Hz), 2.281 (s, 6H), 2.457 (t, 2H, *J*=7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 26.48 (q), 27.42 (t), 29.87 (t), 80.39 (s), 125.12 (d), 128.49 (d), 129.29 (d), 129.78 (d), 133.48 (d), 135.18 (d), 135.88 (s), 200.99 (s); GCMS *m/z* (rel intensity) 546 ($M^{+\cdot}$ 0.7), 274 (4), 235 (4), 218 (7), 207 (10), 193 (25), 192 (28), 175 (12), 165 (6), 123 (16), 110 (26), 109 (100), 91 (10), 83 (11), 77 (10), 69 (19), 65 (32), 51 (10); HRMS calcd for $C_{19}H_{20}O_2S_2Hg$ 546.0611, found 546.0604; Anal. Calcd for $C_{19}H_{20}O_2S_2Hg$: C, 41.87; H, 3.70; S, 11.76. Found: C, 41.97; H 3.72; S, 11.82.

d. 3,3-Diacetyl-3-phenylthiopropyl Phenyl Sulfide (77)



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 2.135 (t, 2H, *J*=8.1 Hz), 2.276 (s, 6H), 2.884 (t, 2H, *J*=8.1 Hz), 7.17-7.39 (m, 10H); GCMS *m/z* (rel

intensity) 344 ($M^{+\cdot}$, 4), 302 (6), 235 (3), 208 (5), 166 (16), 149 (27), 123 (88), 109 (10), 91 (8), 77 (13), 65 (10), 45 (62), 41 (100).

8. General Procedure for the Demercuration of 3,3-Diacetylpropylmercuric Chloride Followed by ^{1}H NMR

3,3-Diacetylpropylmercuric chloride (0.20 mmol) was dissolved in 1.0 mL of nitrogen-purged Me_2SO-d_6. Toluene (0.20 mmol) was introduced into the solution as an internal standard. The solution was divided into two NMR tubes (0.5 mL in each tube) which were equipped with rubber septa. After a ^{1}H NMR spectrum of initial solution was obtained, a deuterated Me_2SO solution of $KOCMe_3$ was syringed into the reaction tube. The progress of the reaction was monitored at different periods of time by ^{1}H NMR integration. The reaction in the presence of 10 mol% of di-*tert*-butyl nitroxide was carried out under the same conditions. The yields of the product at different times are listed in Table XXXII and the data are plotted in Figure IV (see results in section 2 of this chapter)

SUMMARY

Radical chain reactions of alkylmercury halides with electron-deficient alkenes yield the reductive alkylation products in the presence of a silyl hydride in dimethyl sulfoxide. Experimental evidences have been presented that the reaction involves the formation of the alkylmercury hydride as a reactive intermediate. This alkylmercury hydride is both a chain initiator and a hydrogen atom donor in the propagation step. High yields of the alkylation products are observed in 1 to 24 hours in the dark when alkenes are the limiting reagents. The reactions involving silyl hydrides occur readily in dimethyl sulfoxide but not in less polar solvents such as methylene chloride, tetrahydrofuran, or dimethylformamide. This alkylation process is a convenient method for the formation of carbon-carbon bonds. It is an alternative to the sodium borohydride method which is a widely used technique. This new process does not require an excess of alkene as is usually the case with the sodium borohydride method. In reactions where silyl hydrides are used, the low steady state concentration of the alkylmercury hydride makes intermolecular alkylation the predominant reaction course. Furthermore, the large selection of silyl hydrides available allows this method to be more versatile and more controllable than the $NaBH_4$ reductions. Silyl hydride method also has the ability to tolerate a variety of different functional groups including aldehydes.

An important side reaction has been recognized to occur in the reactions of alkylmercury halides and silyl hydrides with terminal alkenes. 1,1-Disubstituted alkenes capable of chelation with alkylmercury halides undergo primarily reduction to yield hydrogenation products of the alkenes.

This new process has been used to study the substituent effects on the reactivities of substituted olefins in radical *tert*-butylation. The relative reactivities of a variety of

substituted alkenes have been measured in competition reactions. The results of the relative reactivity study support the conclusion that *tert*-butyl radical addition to olefins is nucleophilic in character with an early transition state in a kinetic controlled process.

Reactions of 3,3-diacetylpropylmercuric chloride have also been studied. 3,3-Diacetylpropylmercuric chloride is capable of undergoing nucleophilic demercuration in the presence of a strong base. It is also able to undergo radical chain processes upon irradiation in the presence of diphenyl disulfide. The mechanisms involved have been studied in detail.

REFERENCES

1. Frankland, E. *Ann.* **1849**, *71*, 171, 213.

2. Watts, H. *A Dictionary of Chemistry*, London: Longmans, Green, 1887, Vol. 6, p590.

3. Gomberg, M. *J. Am. Chem. Soc.* **1900**, *22*, 757.

4. Paneth, F.; Hofetitz, W. *Chem. Ber.* **1929**, *62*, 1335.

5. Hey, D. H.; Waters, W. A. *Chem. Rev.* **1937**, *21*, 169.

6. Waters, W. A. *Intra-science Chemistry Reports* **1970**, *4*, 77 (M. S. Kharasch Commemorative Issue).

7. Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574.

8. Curran, D. P. *Synlett* **1991**, 63.

9. (a) Kitching, W. *Organomet. React.* **1972**, *3*, 319. (b) Oullete, R. J. in *Oxidation in Organic Chemistry*; pt. B; p140-166; Trahanovsky, W. Ed.; Academic Press: New York, 1973.

10. Giese, B. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 553.

11. Russell, G. A.; Hershberger, J.; Owens, K. *J. Am. Chem. Soc.* **1979**, *101*, 1312.

12. Hershberger, J.; Russell, G. A. *Synthesis* **1980**, 475.

13. Russell, G. A.; Hershberger, J. *J. Am. Chem. Soc.* **1980**, *102*, 7603.

14. Russell, G. A.; Hershberger, J.; Owens, K. *J. Organomet. Chem.* **1982**, *225*, 43.

15. Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398.

16. Russell, G. A.; Tashtoush, H.; Ngoviwatchai, P. *J. Am. Chem. Soc.* **1984**, *106*, 4622.

17. Russell, G. A.; Guo, D. *Tetrahedron Lett.* **1984**, *25*, 5239.

18. Russell, G. A.; Khanna, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 1450.

19. Russell, G. A.; Khanna, R. K. *Tetrahedron Lett.* **1985**, *41*, 4133.

20. Russell, G. A.; Guo, D.; Khanna, R. K. *J. Org. Chem.* **1985**, *50*, 3423.

21. Russell, G. A.; Ngoviwatchai, P. *Tetrahedron Lett.* **1985**, *26*, 4975.

22. Russell, G. A.; Khanna, R. K.; Guo, D. *J. Chem. Soc., Chem. Commun.* **1986**, 632.

23. Russell, G. A.; Ngoviwatchai, P. *Tetrahedron Lett.* **1986**, *27*, 3479.

24. Russell, G. A.; Jiang, W.; Hu, S. S.; Khanna, R. K. *J. Org. Chem.* **1986**, *51*, 5498.

25. Russell, G. A.; Khanna, R. K. *Adv. Chem. Ser.* **1987**, *No.215*, 355.

26. Russell, G. A.; Ngoviwatchai, P.; Tashtoush, H.; Hershberger, J. *Organometallics* **1987**, *6*, 1414.

27. Russell, G. A.; Khanna, R. K. *Phosphorus Sulfur* **1987**, *29*, 271.

28. Russell, G. A.; Ngoviwatchai, P. *Tetrahedron Lett.* **1987**, *28*, 6113.

29. Russell, G. A.; Ngoviwatchai, P.; Tashtoush, H. *Organometallics* **1988**, *7*, 696.

30. Russell, G. A.; Ngoviwatchai, P.; Tashtoush, H.; Pla-Dalmau, A.; Khanna, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 3530.

31. 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.

32. Russell, G. A.; Guo, D.; Baik, W.; Herron, S. *J. Heterocycles* **1989**, *28*, 143.

33. Kurosawa, H.; Okada, H.; Hatlori, T. *Tetrahedron Lett.* **1981**, *22*, 4495.

34. Russell, G. A.; Kim, B. H. *Tetrahedron Lett.* **1990**, *31*, 6273.

35. Nugent, W. A.; Kochi, J. K. *J. Organomet. Chem.* **1977**, *124*, 371.

36. Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1256.

37. Newcomb, M.; Park, S. U. *J. Am. Chem. Soc.* **1986**, *108*, 4132.

38. Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon: Oxford, 1986.

39. Minisci, F.; Citterio, A.; Giordano, C. *Acc. Chem. Res.* **1983**, *16*, 27.

40. Losev, I. P.; Smirnova, O. V.; Bondar, E.; Lutsenco, L. M.; Konazhevski, A. *Izvest. Vysshikh Ucheb. Zavedeni, Khim. Tekhnol.* **1959**, *2*, 589 (*Chem. Abstr.* **1960**, *54*, 7543).

41. (a) Walker, U. S. Patent 2,478,990 (*Chem. Abstr.* **1950**, *44*, 2009). (b) Stewart, J. M.; Chang, C. H. *J. Org. Chem.* **1956**, *21*, 635.

42. Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.

43. Fiesselmann, H.; Ribka, J. *Chem. Ber.* **1956**, *89*, 27.

44. Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633.

45. Bernstein, H. I.; Long, D. U.S. Patent 2,441,130 (*Chem. Abstr.* **1948**, *42*, 5720).

46. Bachman, G. B.; Tanner, H. A. *J. Org. Chem.* **1939**, *4*, 493.

47. (a) Leyendecker, F.; Comte, M.-T. *Tetrahedron Lett.* **1982**, *23*, 5031. (b) Warren, S. *J. Chem. Soc. Perkin Trans. 1* **1986**, 1939.

48. (a) Casey, D. J.; Marvel, C. S. *J. Org. Chem.* **1959**, *24*, 1022. (b) Lukac, I.; Moravcic, M.; Hrdlovic, P. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1913.

49. Overberger, C. G.; Schiller, A. M. *J. Polym. Sci., Part C* **1963**, *1*, 325.

50. Gras, J.-L. *Tetrahedron Lett.* **1978**, *24*, 2111.

51. Davies, C. R.; Davies, J. S. *J. Chem. Soc. Perkin Trans. 1* **1976**, 2390.

52. Chatgilialoglu, C.; Scaiano, J. C.; Ingold, K. U. *J. Organomet. Chem.* **1974**, *71*, 39.

53. Makarova, L. G.; Nesmeyanov, A. N. *Methods of Elemeto Organic Chemistry, Vol 4*, North Holland Publishing Co.: Amsterdam, **1967**.

54. Marvel, C. S.; Gauerke, C. G.; Hill, E. L. *J. Am. Chem. Soc.* **1925**, *47*, 3009.

55. Kharasch, M. S.; Swartz, S. *J. Org. Chem.* **1938**, *3*, 405.

56. Seyferth, D.; Towe, R. H. *Inog. Chem.* **1962**, *1*. 185.

57. DeTar, D. F.; Tenpas, C. J. *J. Am. Chem. Soc.* **1976**, *98*, 4567.

58. Lewis, L. N.; Sy, K. G.; Bryant, G. L., Jr.; Donahue, P. E. *Organometallics* **1991**, *10*, 3750.

59. Bright, D. A.; Mathisen, D. E.; Zieger, H. E. *J. Org. Chem.* **1982**, *47*, 3521.

60. Schmerling, L.; Luvisi, J. P.; Welch, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 1774.

61. Boustany, K. *J. Chem. Eng. Data* **1972**, *17*, 104.

62. Hartmann, J.; Muthukrishnan, R.; Schlosser, M. *Helv. Chim. Acta* **1974**, *57*, 2261.

63. Kim, B. H. *Ph. D. Dissertation*, Iowa State University, Ames, Iowa, **1991**.

64. Bornstein, D.; Weisz, A.; Mandelbaum, A. *Org. Mass Spectrum* **1986**, *21*, 225.

65. Marvel, C. S.; Dec, J.; Cooke, H. G., Jr.; Cowan, J. C. *J. Am. Chem. Soc.* **1940**, *62*, 3495.

66. Blatt, A. H. *Org. Syntheses Coll., Vol. 2,* John Wiley & Sons, Inc.: New York, 1943, p406.

67. Bowden, K.; Heilbron, I. M.; Jones, E. R. H. *J. Chem. Soc.* **1946**, 39.

68. Zimmermann, J.; Seebach D. *Helvetica Chimica Acta* **1987**, *70*, 1104.

69. Baroni, F. E.; Kovyrzina, K. A.; Andreeshchev, E. A. *J. Gen. Chem. USSR,* **1960**, *30*, 2002.

70. Ballesteros, P.; Roberts, B. W.; Wong, J. *J. Org. Chem.* **1983**, *48*, 3603.

71. Naito, I.; Kinoshita, A.; Yonemitsu, T. *Bull. Chem. Soc. Jpn.* **1976, *49***, 339.

72. Anderson, V. K.; Munch-Peterson, J. *Acta Chem. Scand.* **1962**, *16*, 947.

73. Gendreau, Y.; Normant, J. F. *Bull. Soc. Chim. Fr.* **1979**, 305.

74. Brandstrom, A. *Acta Chem. Scand.* **1959**, *13*, 613.

75. (a) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Chem. Lett.* **1987**, 2037. (b) Petit, Y.; Sanner, C.; Larchevegue, M. *Tetrahedron Lett.* **1990**, *31*, 2149.

76. Masuda, Y.; Hoshi, M.; Arase, A. *J. Chem. Soc. Chem. Commun.* **1989**, 266.

77. Yao, C.-F. *Ph. D. Dissertation*, Iowa State University, Ames, Iowa, **1991**.

78. Funabiki, T.; Sato, H.; Tanaka, N.; Yamazaki, Y.; Yoshida, S. *J. Mol. Catal.* **1990**, *62*, 157.

79. Giese, B.; Kretzschmar, G.; Meixner, J. *Chem. Ber.* **1980**, *113*, 2787.

80. McWilliam, D. C.; Balasubramanian, T. R.; Kuivila, H. G. *J. Am. Chem. Soc.* **1978**, *100*, 6407.

81. Taber, D. F.; Amedio, J. C., Jr.; Jung, K.-Y. *J. Org. Chem.* **1987**, *52*, 5621.

82. Oka, K.; Nakao, R. *J. Organomet. Chem.* **1990**, 390, 7.

83. Takaki, K.; Maeda, T.; Ishikawa, M. *J. Org. Chem.* **1989**, *54*, 58.

84. Bordwell, F. G.; Drucker, G. E.; McCollum, G. J. *J. Org. Chem.* **1982**, *47*, 2504.

85. Man, E. H.; Frostick, F. C.; Haceser, C. R. *J. Am. Chem. Soc.* **1952**, *74*, 3228.

86. Souchet, M.; Clark, R. D. *Synlett* **1990**, 151.

87. Glaze, W. H.; Berry, D. J.; Duncan, D. P. *J. Organomet. Chem.* **1973**, *52*, 233.

88. Meyers, A. I.; Kovelesky, A. C.; Jurjevich, A. F. *J. Org. Chem.* **1973**, *38*, 2136.

89. Walling, C. *Free Radicals in Solution*, John Wiley & Sons, Inc.: New York, **1973**, Vol. II, Chapter 14.

90. Espenson, J. H. *Chemical Kinetics and Reaction Mechanism*, McGraw-Hill: New York, 1981, Chapter 3 and 7.

91. Poutsma, M. L. in *Free Radicals*, Kochi, J. K. Ed., John Wiley & Sons, Inc.: New York, **1973**, Vol. II, Chapter 14.

92. Sokolov, V. I.; Bashilov, V. V.; Reutov, O. A. *J. Organomet. Chem.* **1978**, *162*, 271.

93. The absolute rate constant for *tert*-butyl radical addition to CH_2=CHP(O)$(OEt)_2$ at 233 K has been measured as 5.9 x 10^4 $M^{-1}s^{-1}$: Baban, J. A.; Roberts, B. P. *J. Chem. Soc. Perkin Trans. II*, **1981**, 161. Using E_a = 4 kcal/mol yields 4.8 x 10^5 $M^{-1}s^{-1}$ at 35 °C.

94. Rate constants have been reported at 57 °C in H_2O for attack of butyl radical and *tert*-butyl radical upon PyH^+ as 4.4 x 10^4 and 3.3 x 10^4 $M^{-1}s^{-1}$, respectively; Citterio, A.; Minisci, F.; Franchi, V. *J. Org. Chem.*, **1980**, *45*, 4752.

95. Giese, B. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 753.

96. Gottlieb, H. in *The Chemistry of Enones,* Part 1; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989, Chapter 5.

97. Hayes, W. P.; Timmons, C. T. *Spectrochim. Acta* **1968**, *24A*, 323.

98. Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786.

99. (a) Mestres, R.; Palomo, C. *Sunthesis* **1982**, *4*, 288. (b) Matthews, F. W.; Michell, J. H. *Ind. Ehg. Chem., Anal. Ed.* **1946**, *18*, 662.

100. Russell, G. A.; Baik, W.; Ngoviwatchai, P.; Kim, B. H. *Acta Chem. Scand.* **1990**, *44*, 170.

101. Rajaratnam, R. *Ph. D. Dissertation*, Iowa State University, Ames, Iowa, 1992.

102. Ichikawa, K.; Itoh, O.; Kawamura, T. *J. Org. Chem.* **1966**, *31*, 447.

103. Paine, J. B., III; Brough, J. R.; Buller, K. K.; Erikson, E. E.; Dolphin, D. *J. Org. Chem.* **1987**, *52*, 3993.

ACKNOWLEDGMENTS

I am greatly indebted to my major professor, Glen A. Russell, for his helpful guidance and discussions throughout my graduate studies. He has not only taught me many aspects of chemical sciences, but also demonstrated a model for treating people with great respect and tolerance.

I would like to thank other members of my Program of Study Committee, for their time and participation in my degree program: Professor Trahanovsky, Professor Kraus, Professor Johnson, Professor Tipton, and Professor Jenks.

I wish to acknowledge all the members of the Russell group for their friendship and assistance. Thanks also go to Martha for her kindness and care which made my staying in Ames more enjoyable.

Special thanks go to my parents in China, who have given me their constant support and encouragement throughout my education. I am deeply grateful to my wife Yili for her love and sacrifices, and my son James for his smile through the good and bad times.