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Reductive and oxidative alkylations involving free radical chain reactions

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Reductive and oxidative alkylations involving free radical chain reactions

by

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INTRODUCTION

The concept of radicals was introduced by Lavoisier[1] in 1789, and the early nineteenth century saw the discovery of numerous 'radicals'. In the 1840s Kolbe[2] obtained gases, by electrolysis of solutions of fatty acids, which he interpreted as free radicals. Frankland[3] heated zinc with ethyl iodide in a sealed tube and obtained a gas which he believed to be 'free radical'.

$$\underset{\text{'Ethyl iodide}}{'C_4H_5I} + Zn \longrightarrow \underset{\text{Ethyl'}}{C_4H_5} + ZnI'$$

Gomberg's discovery of triphenylmethyl free radical came very unexpectedly in 1900.[4] He set out to prepare hexaphenylethane by the reaction of triphenylmethyl chloride with silver in benzene. In the 1920s Paneth and Hofeditz[5] showed that the less stabilized alkyl radicals also exist and measured the life time of these radicals in the gas phase. Organic synthesis with radicals began in 1937 when Hey and Waters[6] described the phenylation of aromatic compounds by benzoyl peroxide as a radical reaction. In the same year, Kharasch and co-workers[7] recognized that the anti-Markovnikov addition of hydrogen bromide to alkenes proceeds via radical chain process. In the following years, Mayo, Walling, and Lewis discovered the rules of radical copolymerization reactions.[8]

Organomercurials are readily available and organomercury halides have been electrochemically reduced in liquid ammonia at low temperatures to

produce organomercury radicals which, upon warming, decompose to diorganomercury(II) compounds and mercury metal.[9,10]

$$RHgCl + e^- \longrightarrow RHg\bullet + Cl \xrightarrow{\Delta} (1/2)R_2Hg + (1/2)Hg^0$$

Alkylmercurials possess moderate reactivity in electrophilic substitution and low reactivity in nucleophilic attack at carbon.[11] Organomercury halides, the most commonly used organomercurials, have been found to react in homolytic processes involving the corresponding alkyl radical, R•. One of the most widely studied chain reactions of organomercurials has been the alkaline $NaBH_4$ reduction of alkylmercury halides or carboxylates to yield the alkane[12] or products derived from alkyl radical attack upon a suitable coreactant.[13] Both the pyrolysis of R_2Hg and the alkaline $NaBH_4$ reduction of RHgCl are reactions that involve unstable mercury(I) intermediates. An alkylmercury hydride, RHgH, is proposed to be involved in the $NaBH_4$ reduction as shown in Scheme 1.

Scheme 1

Initiation:

$$RHgX + BH_4^- \longrightarrow RHgH$$
$$RHgH \longrightarrow R\bullet + Hg^0 + H\bullet$$

Propagation:

$$R\bullet + RHgH \longrightarrow RH + RHg\bullet$$
$$RHg\bullet \longrightarrow R\bullet + Hg^0$$

The alkyl radicals generated by this method can be trapped by electron deficient olefins (Scheme 2).[14]

Scheme 2

X = Ph, CO_2Me, CN

Y = Ph, CO_2Me, CN, CF_3, SePh, H, etc.

During the past several years, Russell[15-36] has developed a series of free radical alkylations in which RHgX or R_2Hg participates in the propagation step of a chain process that does not usually involve RHg• as an intermediate other than in the initiation step. Alkylmercury halides have proven to be convenient sources of alkyl radicals in these photostimulated chain reactions.

Electron transfer to an alkylmercury halide[15,24] or attack of an electrophilic radical upon the mercury atom,[19,34] generate the alkyl radical (reactions 1 and 2).

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

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

Chain reactions can be achieved if a donor (D•) or acceptor (A•) radical can be formed by further reactions of an alkyl radical which is itself not a strong donor or

acceptor species. Trapping of alkyl radicals by an added radicaphile can lead to chain reaction if the radicaphile derived species will regenerate R• from the alkylmercurial via reactions 1 or 2. Some examples of reactions which provide such radicals or radical ions are listed according to reaction type in A - C (Q• = D• or A•):

(A) S_H2 reactions of R•[28,34,37]

$$R\bullet + Y\text{-}Q \longrightarrow R\text{-}Y + Q\bullet$$

Y-Q = dichalcogenides, H-SPh, H-$SnBu_3$, PhSe-SO_2Ph, Cl-SO_2Ph, *N*-alkyl-1,4-dihydropyridines.

(B) Addition

$$R\bullet + \pi \longrightarrow R\text{-}\pi\bullet$$

(1) R-π• is an acceptor[28]

$$R\text{-}\pi\bullet + RHgX \longrightarrow R\text{-}\pi\text{-}HgX + R\bullet$$

π = CH_2=CHP(O)$(OEt)_2$, CH_2=$CHSO_2Ph$, CH_2=C($C_6H_4NO_2$-*p*)$_2$, CH_2=$CHCH_2OTs$, CH_2=$CHCH_2OP(O)(OEt)_2$, HC≡CPh, HC≡CCO_2Et, HC≡CCOPh, HC≡CCH_2OTS, HC≡$CCH_2OP(O)(OEt)_2$.

(2) R-$\pi^{\bullet}$ is a donor[15,22,24]

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

π = pyridine, $CH_2=C(C_6H_4OMe\text{-}p)_2$, $R^1R^2C=NO_2^-$,
$R^1R^2C=C(O^-)Ph$, Ph_2P^-, $(MeO)_3P$.

(c) Addition - elimination[20,25,27,32,34]

$$R^{\bullet} + \pi\text{-}Q \longrightarrow R\text{-}\dot{\pi}\text{-}Q \longrightarrow R\text{-}\pi + Q^{\bullet}$$

π-Q = PhCH=CHQ or PhC≡CQ (with Q = Cl, Br, I, $PhSO_2$, PhS, HgCl,
$SnBu_3$); PhCOCH=CHCl; $PhSO_2CH=CHSnBu_3$; $MeO_2CCH=CHI$;
$CH_2=CHCH_2Cl(Br, I)$; $HC\equiv CCH_2Cl$.

It is evident that organomercurials have been attracting more attention in recent years, particularly in the field of radical chemistry. Recently there has been considerable interest in synthesis via radical processes and the application of organomercurials in organic synthesis may increase in the future if unique processes can be discovered.

I. REDUCTIVE AND OXIDATIVE ALKYLATIONS OF ENONES BY ALKYLMERCURY HALIDES

A. Reductive Alkylations Involving Electron Transfer

Photostimulated chain reactions of alkylmercury chlorides with many α,β-unsaturated ketones, esters, lactones, and amides occur readily in the presence of iodide ion. In the presence of iodide ion, enolyl radicals can be reduced to the enolate anion (I^- or $RHgI_2^-$ may be the reducing agent) and the chain reaction propagated (reactions 3 and 4[35,36]; A• = electron accepting radical).

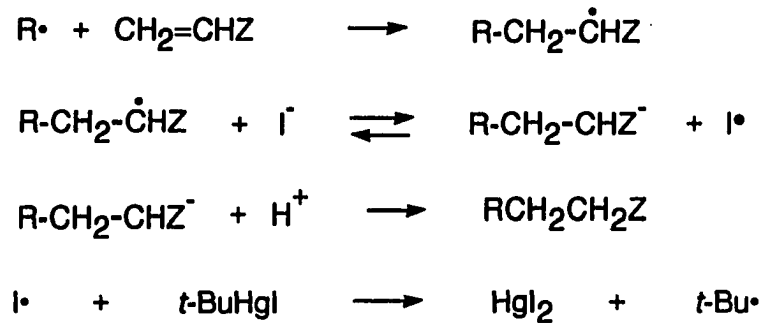
$$A\bullet + I^- \longrightarrow A^- + I\bullet \xrightarrow{t\text{-BuHgI}} HgI_2 + R\bullet \qquad (3)$$

$$A\bullet + RHgI_2^- \longrightarrow A^- + HgI_2 + R\bullet \qquad (4)$$

Thus, the mechanism of photostimulated chains of alkylmercury chlorides with CH=CHZ (Z = electron-withdrawing group) is suggested as shown in Scheme 3.[38]

In addition to the conjugate 1,4 additions of organocopper reagents to α,β-unsaturated ketones,[39-43] the photostimulated conjugate additive (reductive) alkylation by alkyl radicals derived from alkylmercury halides to α,β-unsaturated has proven to be of synthetic utility.

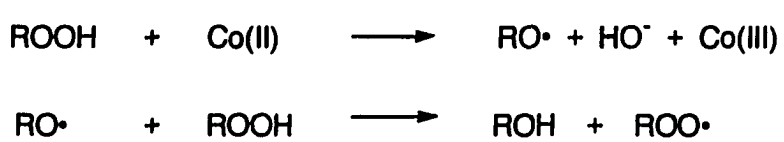
Scheme 3

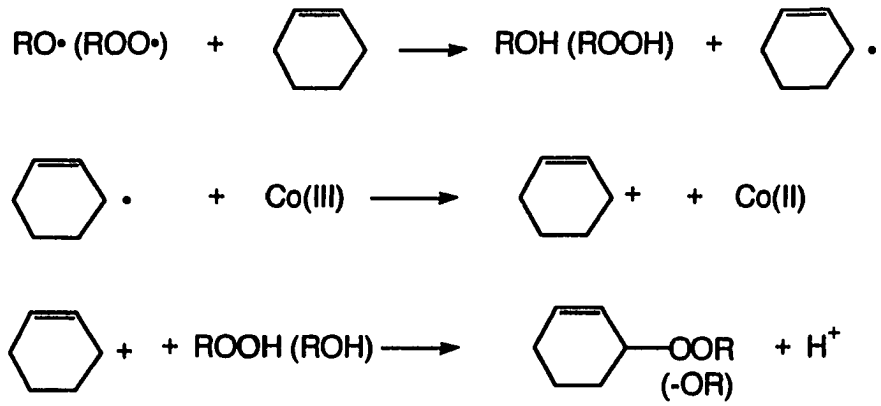


B. Oxidative Alkylations Involving Electron Transfer

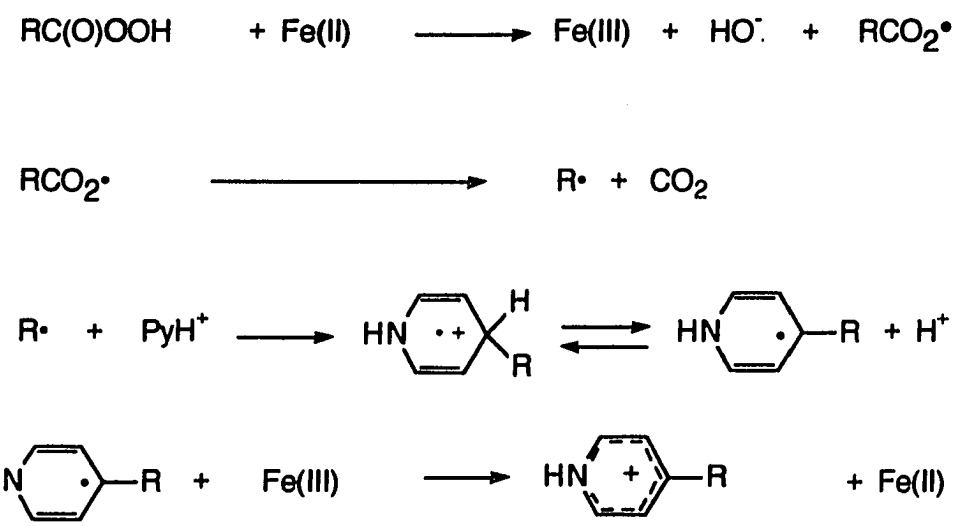
Redox catalysis and electron transfer processes play an important role in selective organic synthesis by free radicals. Metal cations capable of existing in several oxidation states can participate in cyclic processes involving electron transfer wherein the metal ion cycles between two oxidation states. Oxidation-reduction couples such as Fe(II)/Fe(III), Cu(0)/Cu (I), Cu(I)/Cu(II), and Co(II)/Co(III) are effective in a number of such processes.[44] Peroxides, alkyl peresters, or peracids can be forced to react in similar processes such as the Kharasch (Scheme 4)[45] and Minisci (Scheme 5)[46] substitution processes.

Scheme 4

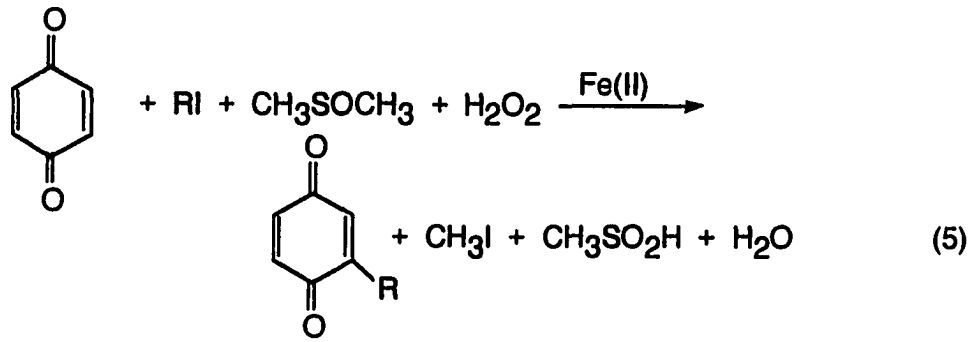




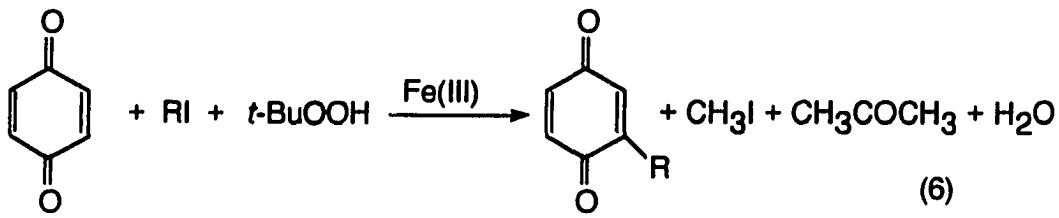
Scheme 5



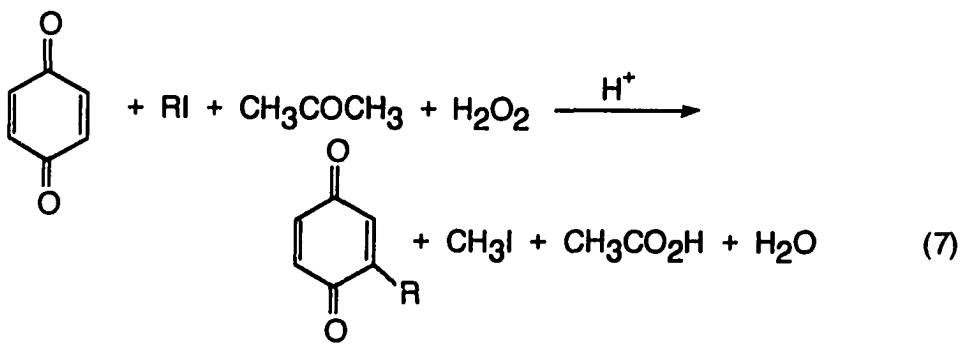
Substitutive (oxidative) free radical alkylations of quinones by *tert*-alkyl iodides has been described in the systems RI/H_2O_2/Fe(II)/Me_2SO, RI/*t*-BuOOH/Fe(III), RI/H_2O_2/Me_2CO/H^+, and RI/$CH_3CO_2^-$/$S_2O_8^{2-}$/H_2O (reactions 5 - 8).[47]


+ RI + CH3SOCH3 + H2O2
Fe(II)
+ CH3I + CH3SO2H + H2O
R

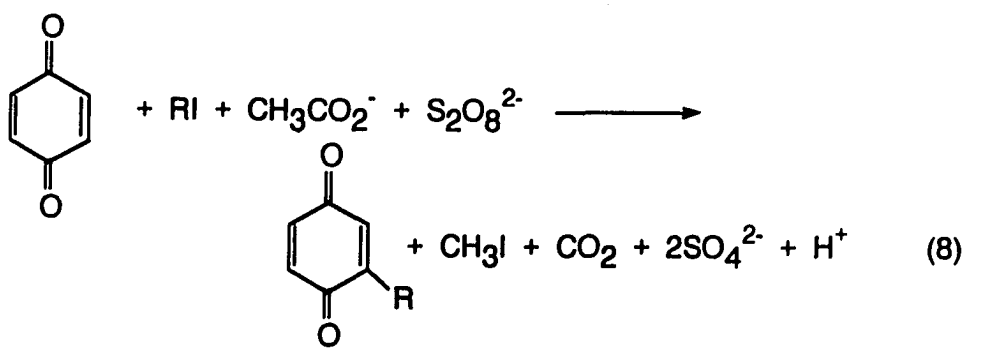
(5)


+ RI + t-BuOOH
Fe(III)
+ CH3I + CH3COCH3 + H2O
R

(6)

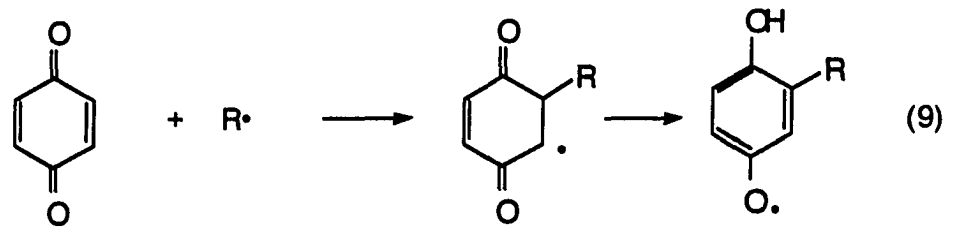

+ RI + CH3COCH3 + H2O2
H+
+ CH3I + CH3CO2H + H2O
R

(7)

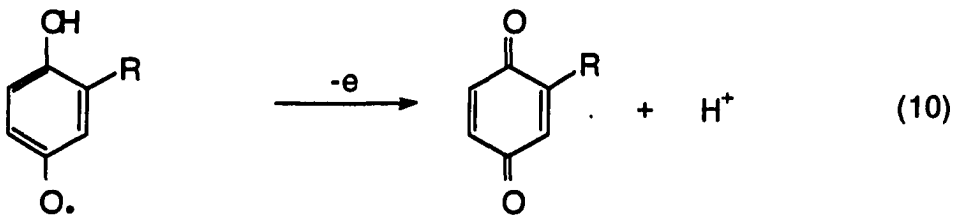

+ RI + CH3CO2- + S2O8 2-
+ CH3I + CO2 + 2SO4 2- + H+
R

(8)

In the above cases chain processes involve the addition of the radical R• to the quinone (reaction 9) and the oxidation of the radical adduct (reaction 10).



(9)



(10)

It has also been demonstrated the the reaction of trialkylboranes with 1,4-quinones to form upon hydrolysis the 2-alkylhydroquinones proceeds by a free radical chain mechanism.[48]

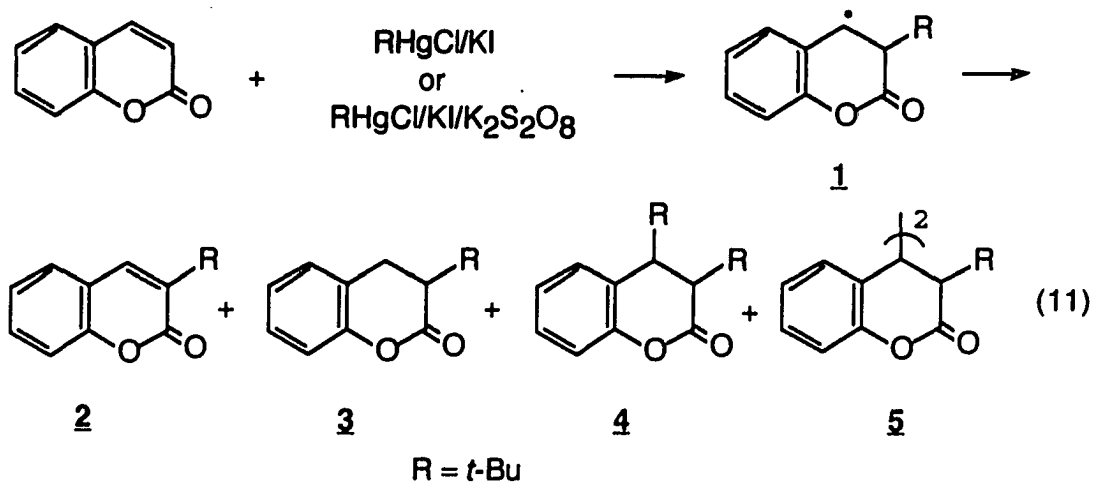
In this chapter, the photostimulated reaction of alkylmercury halides with various substrates for reductive and oxidative alkylations will be discussed.

C. Results and Discussion

1. Photostimulated reactions of alkylmercury halides with coumarin

Photostimulated chain reactions of alkylmercury chlorides with α,β-unsaturated ketones produce additive (reductive) product in the presence of iodide ion. However, α,β-unsaturated compounds such as coumarin react with alkyl radicals by α-attack to generate the benzylic radical, which reacts slowly or

not at all with RHgCl. In the presence of KI or KI/$K_2S_2O_8$, a complex reaction mixture is formed which includes the coupling product of 1 with a second *t*-Bu•, 3-*tert*-butyldihydrocoumarin, a small amount of 3-*tert*-butylcoumarin, and four (two major and two minor) diastereomeric dimerization products of 1 (reaction 11). A similar product distribution but with one of the diastereomers predominating was observed from the reaction with (*t*-Bu)$_2$Cu(CN)Li$_2$ in THF -78 °C in a process which apparently also proceeds by the intermediacy of 1.



The persulfate/iodide system rapidly forms *t*-Bu• by the attack of I• and $SO_4^{\bullet-}$ upon *t*-BuHgCl as evidenced from CIDNP signals for $Me_2C{=}CH_2$ and Me_3CH formed by the diffusive encounter of two *t*-Bu• in the absence of a radical trap.[35]

Scheme 6

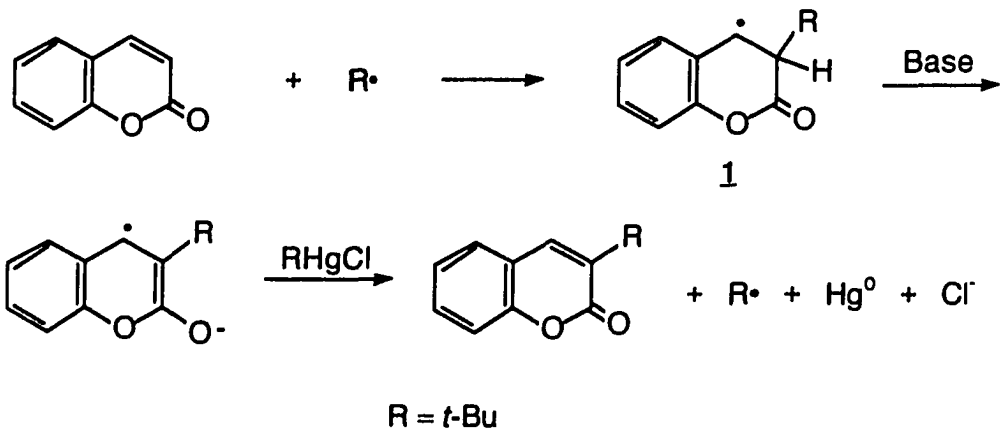
$$I^- + S_2O_8^{2-} \longrightarrow I\bullet + SO_4^{2-} + SO_4^{\bullet-}$$

$$I\bullet + RHgX \longrightarrow R\bullet + IHgX$$

$$SO_4^{\bullet-} + RHgX \longrightarrow R\bullet + XHgOSO_3^-$$

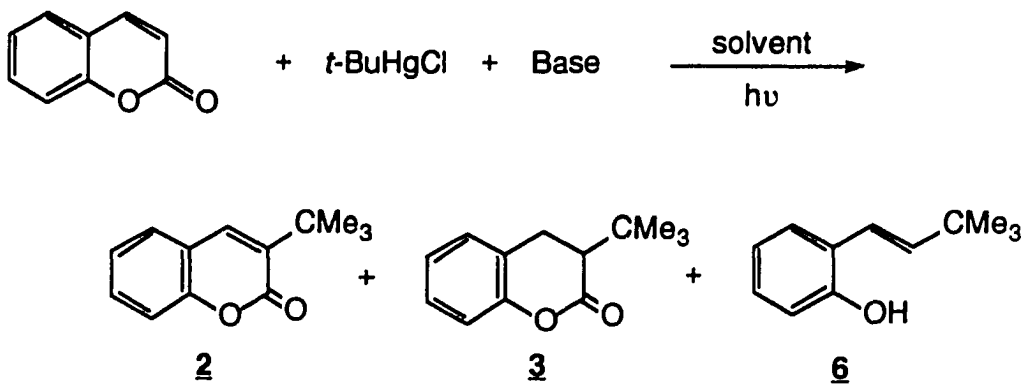
Even though coumarin reacts with alkyl radicals by α-attack to generate the benzylic radical, which reacts slowly or not at all with *t*-BuHgCl, a chain reaction can still be achieved because the adduct radical has an acidic α-hydrogen atom. Addition of base in Me_2SO gives rise to substitutive alkylation to form 3-*tert*-butylcoumarin (2) by the mechanism of Scheme 7. Loss of a proton from 1 generates a powerful reducing species (E_0 = -1.6 V) which continues the chain by electron transfer to RHgCl (E_0 values for variety of alkylmercury acetates in MeOH/H_2O are ~-0.2 V).[49]

Scheme 7



To find the best condition for the oxidative alkylation of coumarin, various kinds of solvents and bases were tried. The combination of 1,4-diazabicyclo[2.2.2]octane (Dabco)/Me_2SO shows the best result for the oxidative alkylation (Table I). Under certain conditions, such as with *t*-BuHgCl/KOH in Me_2SO, coumarin reacts to give a mixture of 3-*tert*-butylcoumarin (**2**) and (*E*)-*o*-$HOC_6H_4CH{=}CHCMe_3$ (**6**) (Scheme 8)

Scheme 8



o-Hydroxycinnamic acid under the same conditions gives the decarboxylated alkene in 50% (Me_2SO) to 60% (DMF) yield upon photolysis (reaction 12).

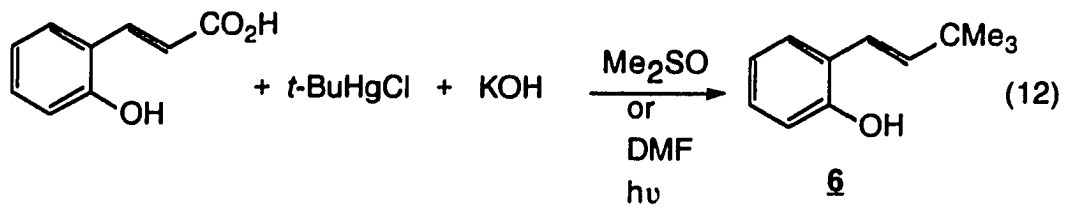


Table I. Selection of proper base and solvent for the oxidative alkylation of coumarin[a]

base	solvent	time (hr)	% yield[b]		
			2	3	6
KOH	Me_2SO	21	66	-	11
KOH	DMF	4.5	14	-	51
Bu_4NF	Me_2SO	4	5	-	27
Bu_4NF	DMF	4	16	-	54
Dabco	**Me_2SO**	**12**	**90**	**<9**	-
Dabco	DMF	7.5	50[c]	tr	-
Dabco	PhH	24	10[c]	-	-
t-BuOK	Me_2SO	21	14	-	27
t-BuOK	DMF	12	17	10	7
t-BuOK	HMPA	12	4	-	3
NaOMe	Me_2SO	0.75	22	-	11
Et_3N	Me_2SO	19	5[c]	-	-
DBU	Me_2SO	5.5	16	-	-
$PhCH_2N(Me)_3OH$	Me_2SO	7	24	-	-
NaOAc	Me_2SO/AcOH	27	no reaction		

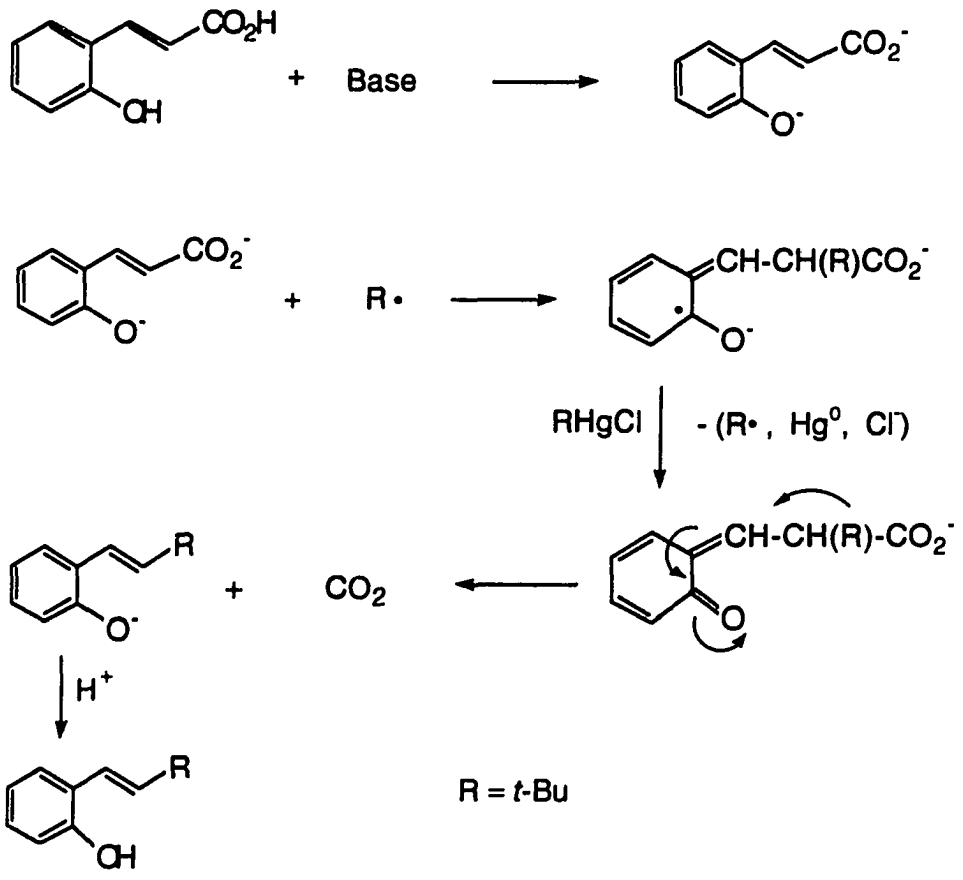
[a]Reactions of 0.5 mmol of coumarin with 4 equiv of *t*-BuHgCl and 4 equiv of base in 10 ml solvent with 275-W fluorescent sunlamp irradiation at ~40 °C.

[b]By GC with toluene as an internal standard.

[c]Starting material recovered (50 - 67%).

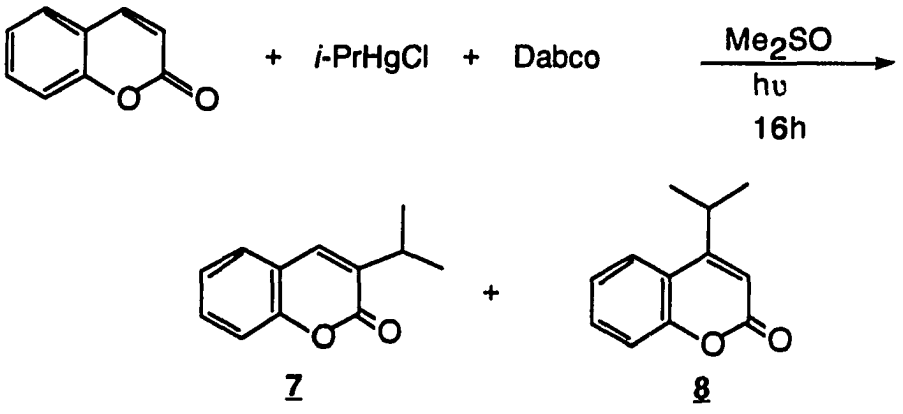
This reaction apparently involves a vinylic S_{RN} process[15] followed by decarboxylation (Scheme 9). Cinnamic acid failed to react, but *p*-hydroxycinnamic acid gives *p*-$HOC_6H_4CH{=}CHCMe_3$ in 60% (Me_2SO) to 71% (DMF) yield.

Scheme 9



For the alkylation of coumarin, addition of Dabco in Me_2SO gives rise to oxidative alkylation to form 3-*tert*-butylcoumarin in 90% yield and it is the best condition among various bases and solvents investigated. With *i*-PrHgCl/Dabco, coumarin

produces 3-isopropylcoumarin (70%) as a major product and the regioisomer 4-isopropylcoumarin (15%).



7 8 (13)

The reaction with *i*-PrHgCl occurred more slowly than with *t*-BuHgCl, presumably because the electron transfer to *i*-PrHgCl is less exergonic than with *t*-BuHgCl. This would be expected if the electron transfer is a dissociative process leading directly to the alkyl radical. The isopropyl radical also reacts with coumarin with a lower regioselectivity than *t*-Bu•.

2. Photostimulated reactions of alkylmercury halides with *N*-methylmaleimide.

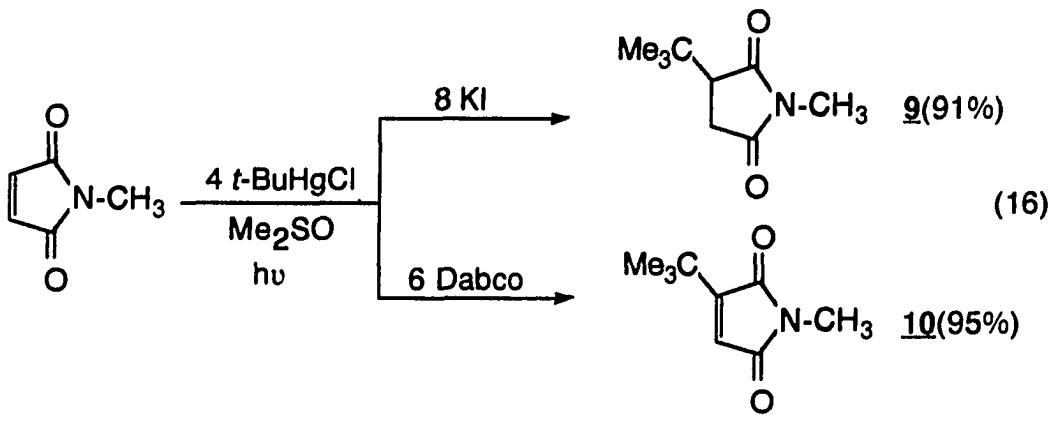
Russell and co-workers have previously reported that enolyl-type radicals are readily converted to the saturated alkylation products in the presence of $RHgCl/I^-$ in Me_2SO.[35] One interpretation of this effect involves eq. 14.

$$>C(R)\dot{C}HC(=O)Z + RHgI_2^{\cdot} \longrightarrow >C(R)CHC(=O^-)Z + R\bullet + HgI_2 \quad (14)$$

In the case of coumarin, a radical of the type $>\dot{C}CH(R)C(=O^-)Z$, which fails to propagate a chain reaction with RHgCl, can be coerced to react in the presence of a base such as Dabco via the formation of a powerful reducing radical anion, eq. 15.

$$>\dot{C}C(R)=C(O^-)Z \quad + \quad RHgX \longrightarrow \quad >C=C(R)C(=O)Z \quad + \quad R\bullet \quad + \quad Hg^0 \quad + \quad X^- \qquad (15)$$

The *tert*-butylation of *N*-methylmaleimide by these techniques allows either the reductive or oxidative alkylation product to be formed exclusively and in high yields.



(16)

The possible E2 pathway for the oxidative alkylation is excluded by following experiment. After the irradiation of *N*-methylmaleimide (1 equiv)/*t*-BuHgI (4)/Me_2SO for 20 min, Dabco (4) was added in the dark and the reaction mixture stirred for an additional 3 hours in a dark condition at ~40 ^oC. After the work up, the only product observed was the saturated compound **9** (51%) without any of **10** (Scheme 10).

Results for reductive and oxidative alkylations of *N*-methylmaleimide are summarized in Table II.

Scheme 10

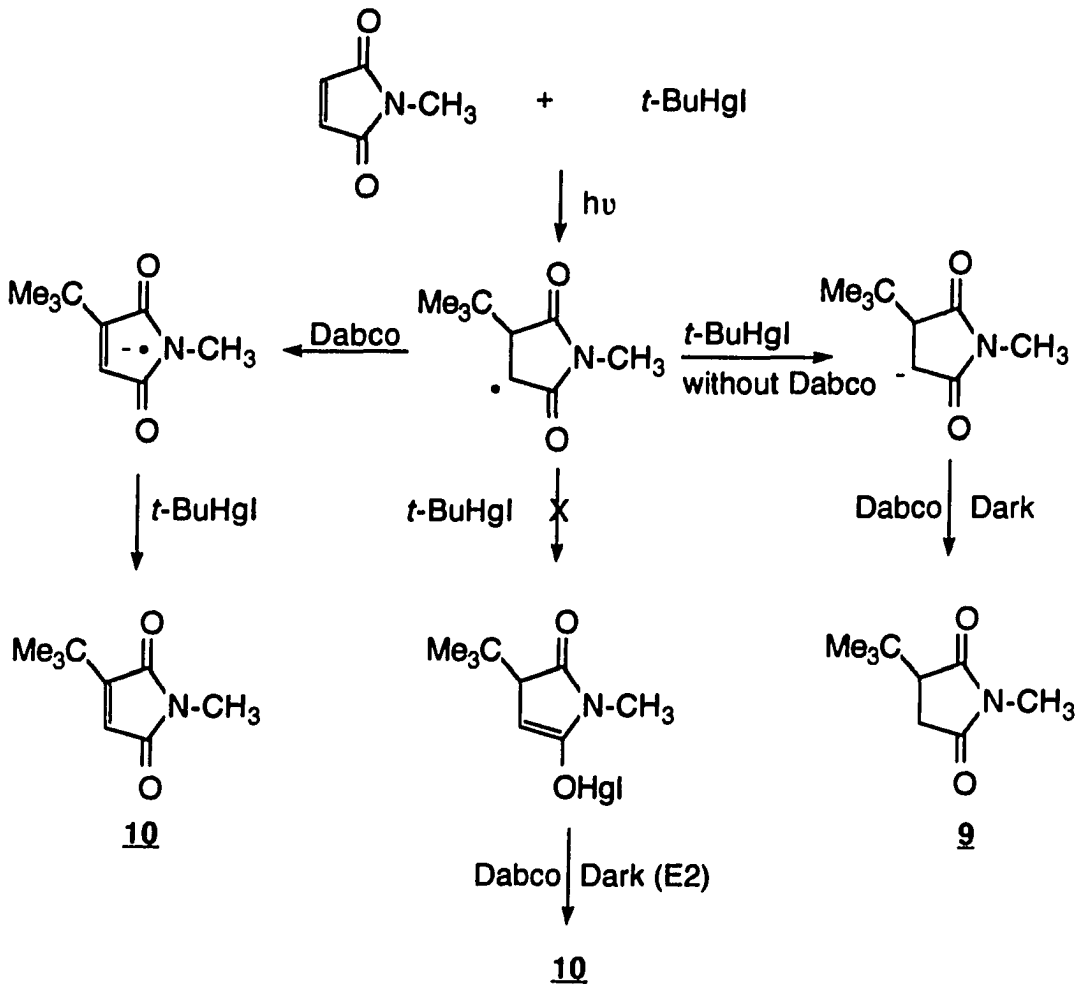
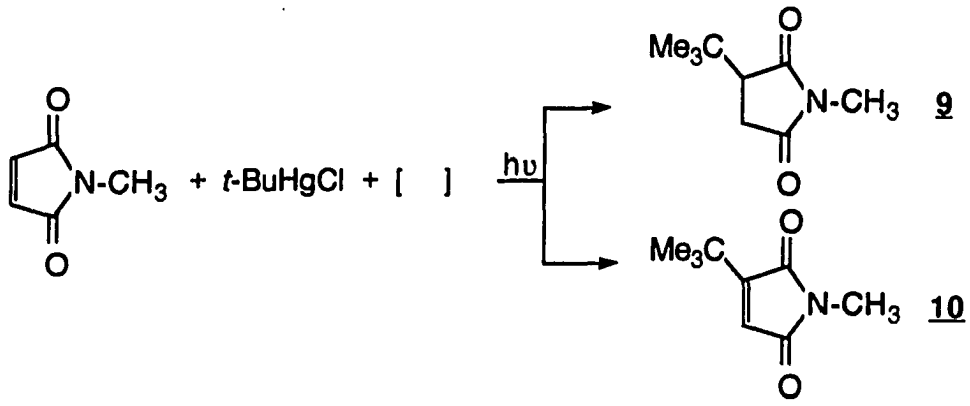


Table II. Alkylation of *N*-methylmaleimide by *t*-BuHgCl in the presence of KI, $K_2S_2O_8$, and Dabco in Me_2SO[a]

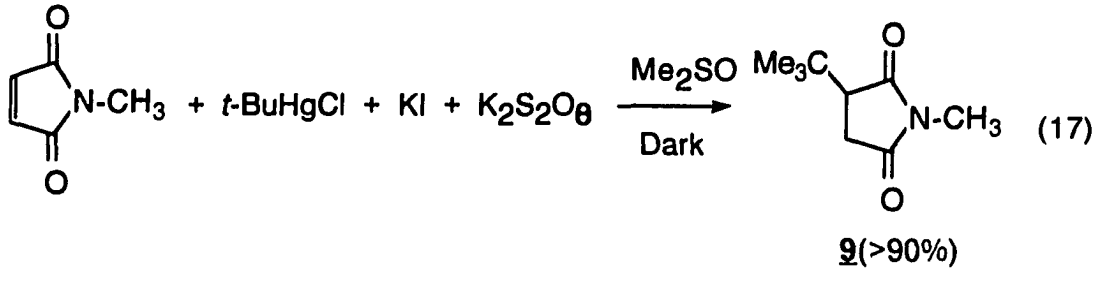


molar equivalents	solvent	% yield(time, h)[b]	
t-BuHgCl:KI:$K_2S_2O_8$:Dabco		9	10
4 : 0 : 0 : 0	Me_2SO	37 (14)	
4 : 0 : 0 : 0	PhH	27 (14)	
4 : 4 : 0 : 0	Me_2SO/MeOH[c]	73 (3.5)	
4 : 8 : 0 : 0	Me_2SO	91 (5 min)	
4 : 0 : 2 : 0	Me_2SO	23 (3.5)	
4 : 4 : 2 : 0	Me_2SO	99 (20 min)	
4 : 4 : 2 : 4	Me_2SO	58 (5)	9 (5)
4 : 0 : 0 : 6	Me_2SO	tr	95 (6)
4 : 8 : 0 : 4	Me_2SO	99 (20 min)	

[a]0.5 Mmol 0f *N*-methylmaleimide in 10 ml of Me_2SO irradiated at ~40 °C with a 275-W GE sunlamp.

[b]By GC with toluene as an internal standard. [c]10 Ml : 1 ml.

Photolysis of *t*-BuHgCl and the imide in Me_2SO gives a low yield of the saturated product (37%) accompanied by by-products. Photolysis in the presence of $K_2S_2O_8$ yields mainly polymeric product but $K_2S_2O_8$/KI gives a quantitative yield of the saturated product. Iodide ion promotion involves an increased rate of photoinitiation from ligand exchange and complexation leading to the more labile *t*-BuHgI and *t*-$BuHgI_2^-$ (complexation constant ~1 M^{-1})[35]. That these species also lead to a faster conversion of the enolyl radical to the enolate product is demonstrated by the observation that for *N*-methylmaleimide a mixture of KI (8 equiv) and Dabco (4 equiv) gives only the saturated product whereas in the absence of KI only the unsaturated product is observed. Reduction of the enolyl radical is believed to involve $RHgI_2^-$. In the presence of $I^-/S_2O_8^{2-}$, the excellent yield of reductive alkylation is believed to occur because the $I^-/S_2O_8^{2-}$ combination leads to a fast rate of initiation from the reactions in Scheme 6 (page 13), and an excellent yield (>90%) of the saturated alkylation product is observed even in the dark (~40 °C for 15 min.).

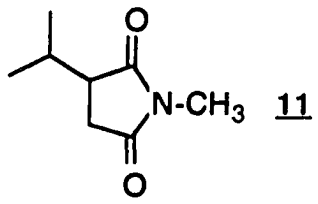


(17)

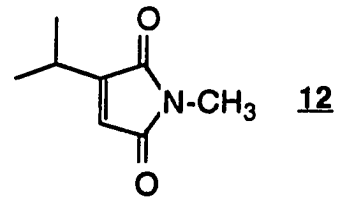
9(>90%)

With *i*-PrHgCl and KI yields of the reductive alkylation product are lower, presumably because *i*-PrHgCl reacts more slowly with electrophilic radical. The relative reactivities of *t*-BuHgCl, *i*-PrHgCl, and *n*-BuHgCl are 1.0 : 0.07 : 0.014

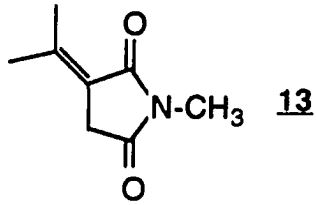
towards $RCH_2\dot{C}HP(O)(OEt)_2$ and 1.0 : 0.08 : 0.014 towards PhS•.[38] This indicates that the rate of homolytic displacement of R• from RHgCl (eq. 2) increases from R = *n*-Bu to *i*-Pr to *t*-Bu, i.e. with the stability of the incipient radical. However, with *i*-PrHgCl/KI or *i*-PrHgCl/KI/$K_2S_2O_8$ only the reductive alkylation product (11) is observed (Table III). Oxidative alkylation with *i*-PrHgCl/Dabco formed a mixture of 12 - 14, and with both KI and Dabco present a mixture of 11 - 14 is observed depending upon the reaction condition (Table III).



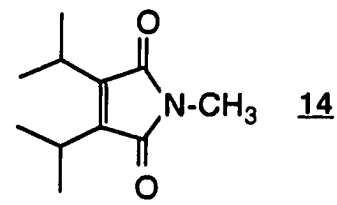
11



12



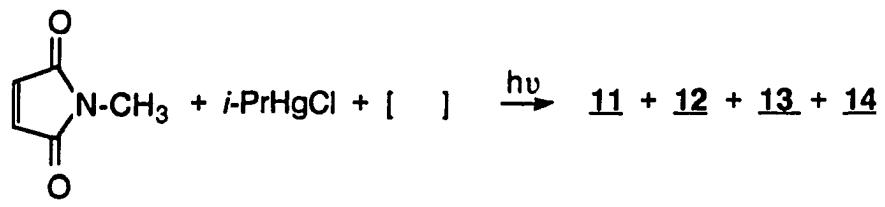
13



14

With a mixture of 4 equiv of *i*-PrHgCl, Dabco, KI, and 2 equiv of $K_2S_2O_8$, a good yield of the doubly alkylated product,14 is formed by further alkylation of unsaturated monoalkylated product 12 (Scheme 11).

Table III. Alkylation of *N*-methylmaleimide by *t*-BuHgCl in Me_2SO[a]

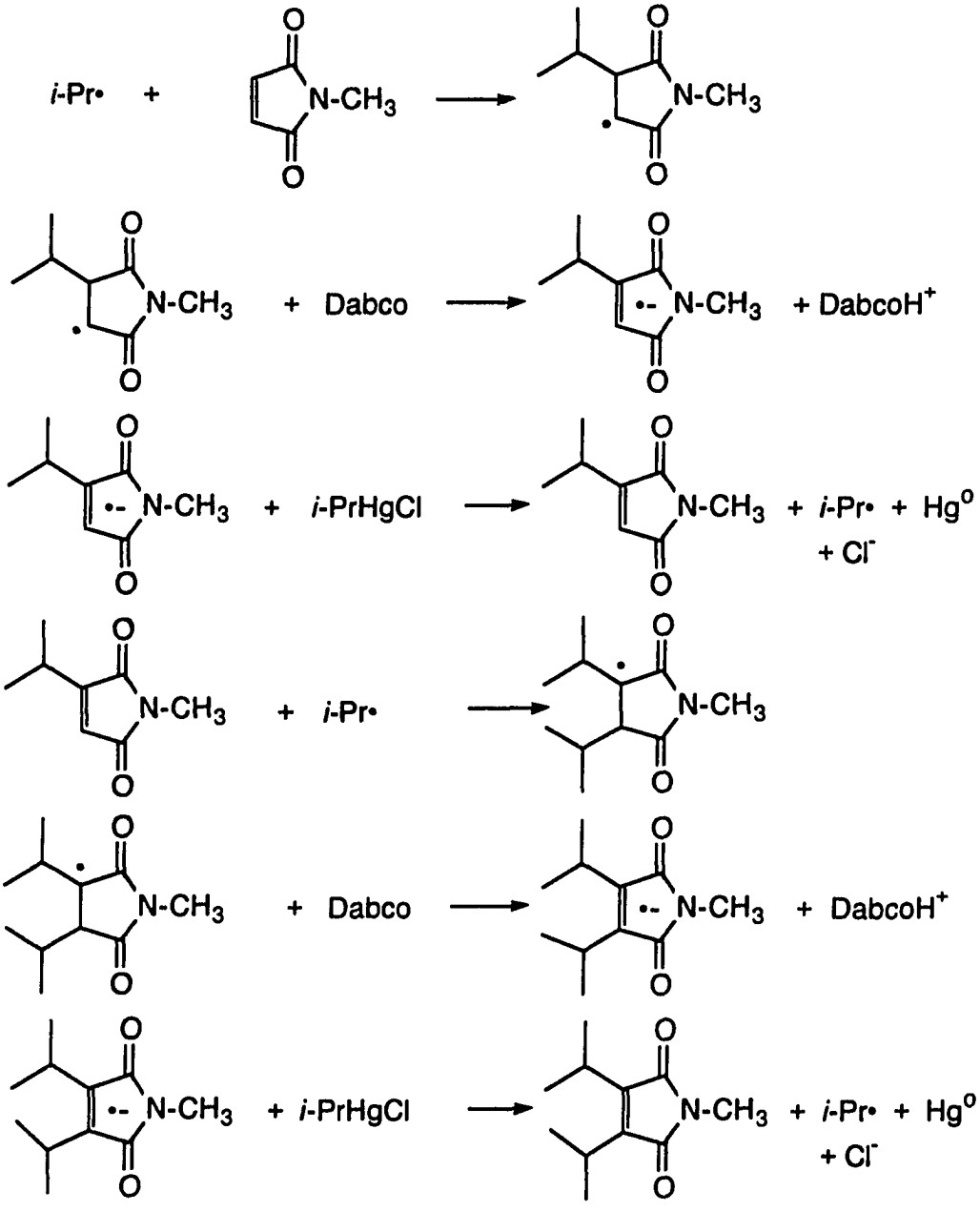


molar equivalents	time (h)	% yield[b]			
i-PrHgCl:KI:$K_2S_2O_8$:Dabco		11	12	13	14
4 : 0 : 0 : 0	10	tr	-	-	-
4 : 8 : 0 : 0	8	30	-	-	-
4 : 4 : 2 : 0	4	32	-	-	-
4 : 0 : 0 : 8	24	-	22	3	14
4 : 4 : 0 : 4	12	14	-	2	27
4 : 4 : 2 : 4	12	14	-	tr	57
4 : 4 : 2 : 8	7	7	6	17	35

[a]0.5 Mmol of *N*-methylmaleimide in 10 ml of Me_2SO irradiated at ~40 °C with a 275-W GE sunlamp.

[b]By GC with toluene as an internal standard.

Scheme 11

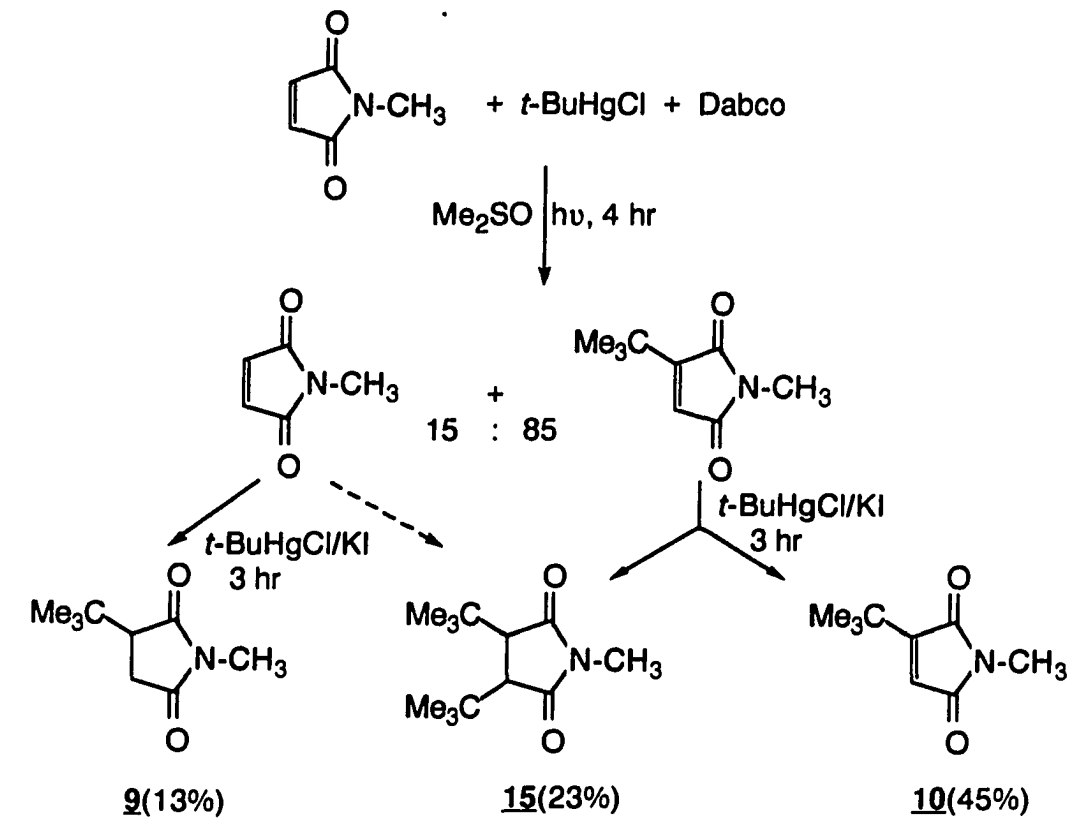


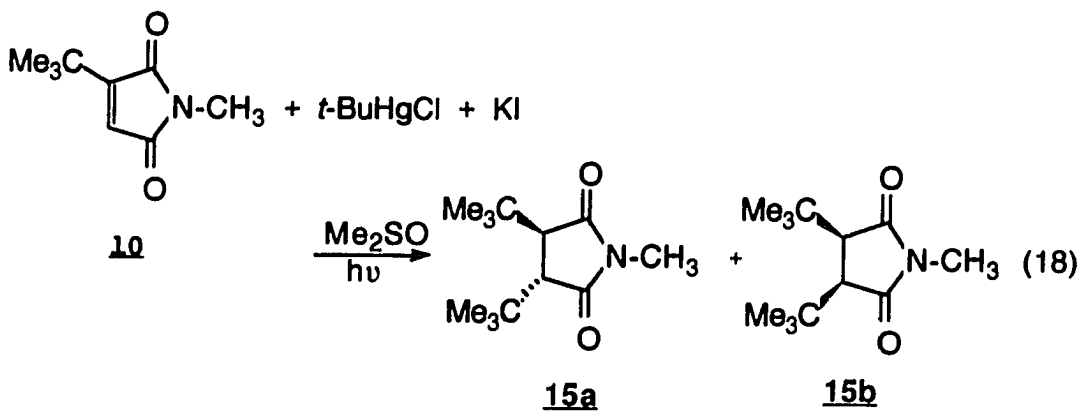
3. Further alkylations of the oxidative alkylation product of *N*-methylmaleimide

As seen in the result of *i*-PrHgCl reactions with *N*-methylmaleimide, dialkylation can also occur. In case of *t*-BuHgCl reactions, *tert*-butylation of *N*-methylmaleimide allows the reductive or oxidative mono-alkylation product to be formed exclusively and in high yield. However, by combining of oxidative and reductive alkylation reaction condition in a proper time sequence, dialkylation can be observed. After a 4 hour irradiation of *N*-methylmaleimide (1 equiv)/*t*-BuHgCl (4 equiv)/ Dabco (4 equiv) in Me_2SO (a separate ^1H NMR experiment showed the ratio of *N*-methylmaleimide : 3-*tert*-butyl-*N*-methylmaleimide= 15 : 85), KI (4 equiv) was added to the reaction mixture and the irradiation continued for 3 hours. The reaction product was now a mixture of 9 (13%) 10 (45%) and 15 (23%, trans and cis) as shown Scheme 12.

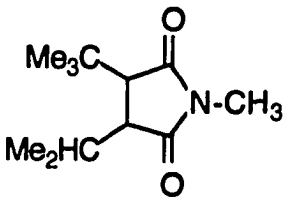
Photolysis of isolated 10 with *t*-BuHgCl (4 equiv)/KI (8) forms only the saturated product 15 (71% in 3 h) as a 2.5 : 1 ratio of cis and trans isomers. Cis-15 does not isomerize to trans-15 under the reaction conditions, but isomerization is observed in KOAc/MeOH to give a cis/trans ratio of ~1:100 (2 days at room temperature) and in Dabco/*t*-BuHgCl/Me_2SO to give a cis/trans ratio of 33 : 67 (1 day at 35 - 40 ^oC) even though the energy barrier for cis-trans isomerization is presumed to be quite high (isomerization in pyridine/CH_2Cl_2, *para*-toluenesulfonic acid (PTSA)/CH_2Cl_2, and PTSA/CH_2Cl_2•Me_2SO is not observed). Reaction of 10 with *t*-BuHgCl/Dabco also formed mainly the saturated product 15 (reaction 18) in 42% yield with a trans/cis ratio of 5. The unsaturated analogue of 15 is observed in the presence of Dabco, but only in low yield.

Scheme 12

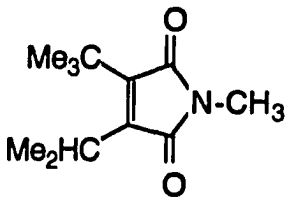

+ t-BuHgCl + Dabco
Me2SO hυ, 4 hr
15 : 85
t-BuHgCl/KI
3 hr
t-BuHgCl/KI
3 hr
9(13%)
15(23%)
10(45%)


+ t-BuHgCl + KI
10
Me2SO
hυ
15a
15b
(18)

The results suggest that formation of 15 from 10 even in the presence of KI now involves hydrogen transfer to the least hindered side of the adduct radical, possibly from R•. This is supported by the observations that workup with D_2O incorporates no more than 10% of deuterium in the isolated 15. The results for the alkylation of 10 by *t*-BuHgCl are summarized in Table IV.



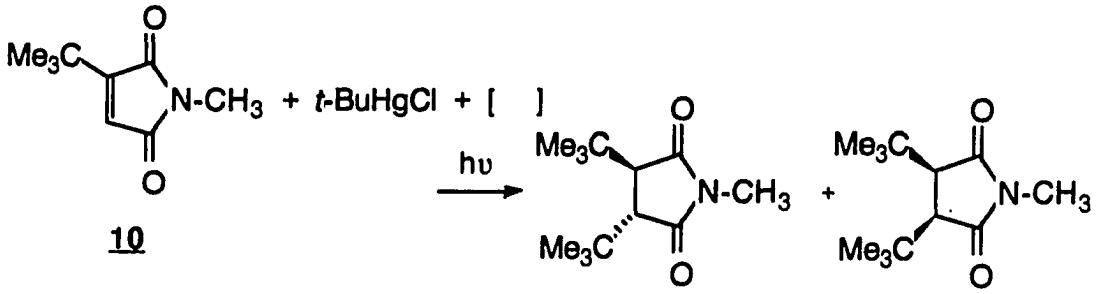
16



17

With *i*-PrHgCl, 10 forms a mixture of saturated (16) and unsaturated (17) products. The trans-cis ratio product ratio for 16 is variable. With Dabco present the oxidative alkylation product (17) predominated but significant amounts of 16 are also formed. In the absence of Dabco but presence of KI the major product is the saturated alkylation product with a predominance of the trans isomer (Table V). With this hindered system probably the saturated products (cis and trans-16) are formed by both electron transfer from *i*-$PrHgI_2^-$ and by radical/radical (termination) reactions. Isomerization of cis-16 to the more stable trans-16 may also be involved.

Table IV. Alkylation of 3-*tert*-butyl-*N*-methylmaleimide (10) by *t*-BuHgCl in Me_2SO[a]



10 15a 15b

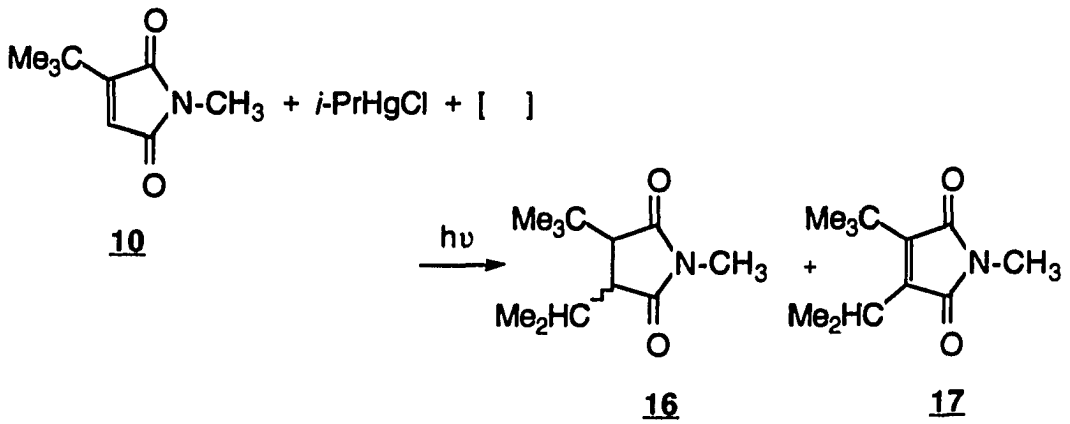
molar equivalents	time (h)	% yield[b]	
t-BuHgCl:KI:$K_2S_2O_8$:Dabco		15a	15b
4 : 8 : 0 : 0	3	21	50
4 : 8 : 2 : 0	20	20	33
4 : 0 : 0 : 4	20	35[c]	7[c]

[a]0.5 Mmol of 10 in 10 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]By GC with toluene as an internal standard.

[c]Di-*tert*-butyl-*N*-methylmaleimide (15%) formed.

Table V. Alkylation of 3-*tert*-butyl-*N*-methylmaleimide (10) by *i*-PrHgCl in Me_2SO[a]



molar equivalents	time (h)	% yield[b]	
i-PrHgCl:KI:$K_2S_2O_8$:Dabco		16 (trans:cis)	17
4 : 8 : 0 : 0	5	51 (5:1)	11
4 : 8 : 0 : 4	5	39 (2:1)	55
4 : 4 : 2 : 0	8	31 (3:1)	5

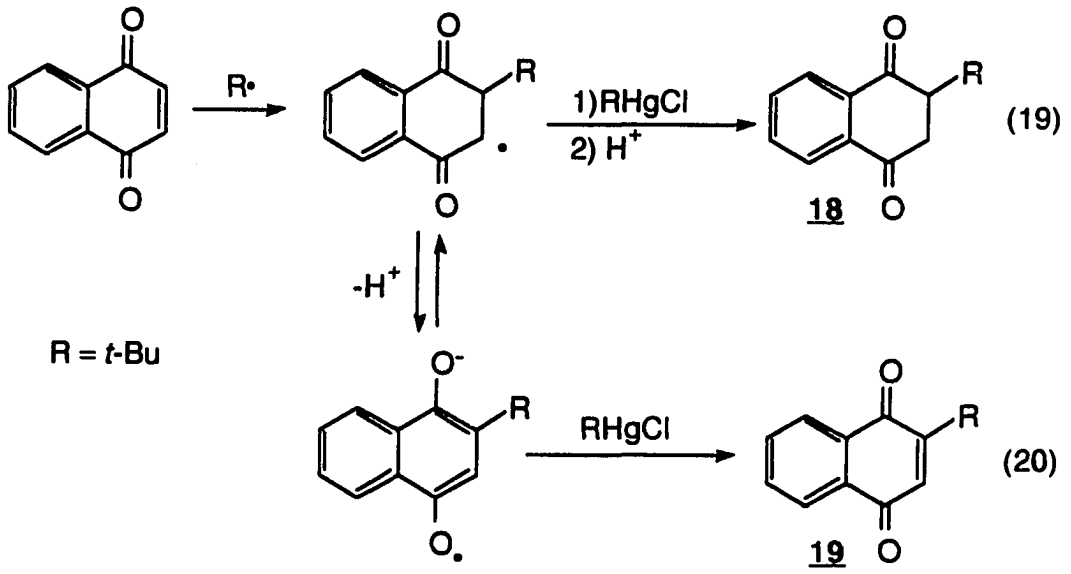
[a]0.5 Mmol of 10 in 10 ml of Me_2SO irradiated at ~40 °C with a 275-W GE sunlamp.

[b]By GC with toluene as an internal standard.

4. Photostimulated reactions of alkylmercury halides with 1,4-naphthoquinone

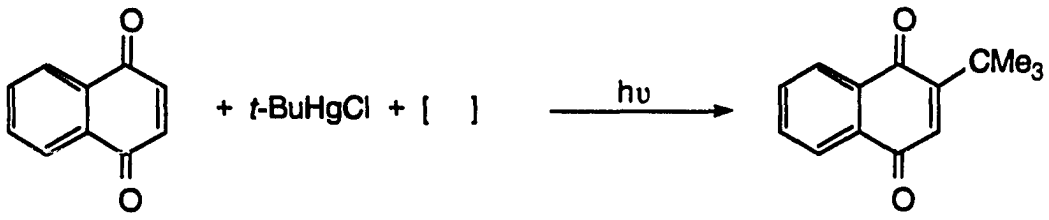
With quinones the adduct radicals generated from the photostimulated reactions are quite acidic and competition between reactions 19 and 20 can be observed with *t*-BuHgCl (Scheme 13).

Scheme 13



The free radical *tert*-butylation of 1,4-naphthoquinone by *t*-BuHgCl can be controlled to give either the reductive (**18**) or the oxidative (**19**) product by the proper choice of proton donor/acceptor. Photolysis in Me_2SO, however, shows poor results as shown in Table VI. In all conditions, a polymerized black tarry product is produced as a major product and **19** is produced with a low yield.

Table VI. Alkylations of 1,4-naphthoquinone by *t*-BuHgCl in Me_2SO



19

conditions[a]	% yield of 19[b]
17 h	6
20 h, 5 vol% H_2O	14
10 h, 5 vol% AcOH	10
36 h, 1 equiv of Dabco	6
19 h, 4 equiv of $(NH_4)_2S_2O_8$, NaI[c]	35

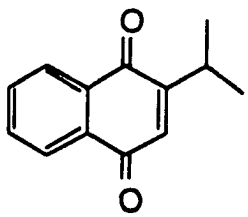
[a]Reaction of 0.5 mmol of 1,4-naphthoquinone with 4 equiv of *t*-BuHgCl in 10 ml of Me_2SO with 275-W GE sunlamp at ~40 °C.

[b]GC yield with toluene as an internal standard.

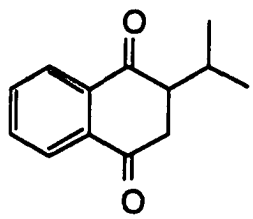
[c]In room right at 25 °C.

However, photolysis in nonpolar PhH gives good results. Photolysis of 1,4-naphthoquinone/*t*-BuHgCl in PhH leads to a mixture of **18** and **19** where **18** exists completely in the diketone form. In PhH (Table VII), reactions leading exclusively to **18** are observed in the presence of proton donors such as H_2O, HOAc, or $(NH_4)_2S_2O_8$. The mixture of products observed in PhH without a proton donor is apparently due to semiquinone formation (Scheme 13). As predicted from Scheme 13, addition of a base such as Dabco causes the reaction product to change completely, and only the substituted quinone **19** is formed in a slow reaction because of the poor driving force for the transfer of an electron from $\mathbf{19}^{\bullet-}$ (E_0 ~0) to *t*-BuHgCl.

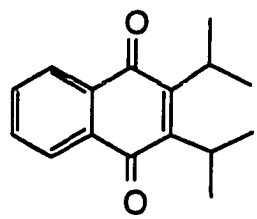
With *i*-PrHgCl in Me_2SO, as with *t*-BuHgCl, reductive alkylation is not observed under various conditions (Table VIII).



20



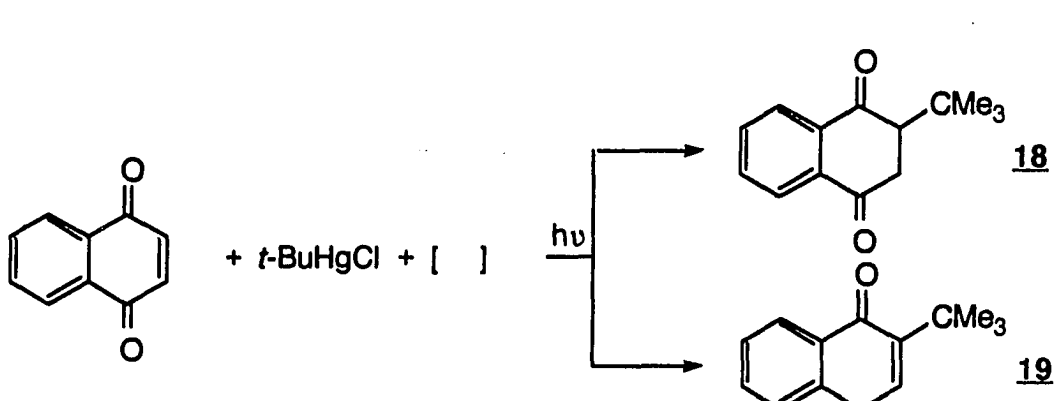
21



22

In Me_2SO, **20** is a major product in all conditions. In benzene, with or without a proton donor, the mixture of **20** and **21** is observed with a ratio varying from ~1 : 1 to ~1 : 3 (**20** : **21**) depending on the reaction condition.

Table VII. Photostimulated reactions of *t*-BuHgCl with 1,4-naphthoquinone in benzene

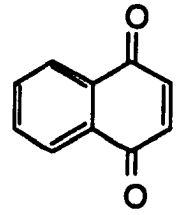


conditions[a]	% yield[b]	
	18	**19**
15 h	14	39
15 h, 4 vol% H_2O	74	0
16 h, 4 vol% HOAc	78	0
17 h, 4 equiv of $(NH_4)_2S_2O_8$	95	0
24 h, 8 equiv of NaI	52	9
24 h, 2 equiv of Dabco	0	47
28 h, 2 equiv of $K_2S_2O_8$, 1.2 equiv of Dabco	0	47

[a]Reaction of 0.5 mmol of 1,4-naphthoquinone with 4 equiv of *t*-BuHgCl in 12 ml of benzene with 275-W GE sunlamp irradiation at ~40 °C.

[b]GC yield with toluene as an internal standard.

Table VIII. Photostimulated reactions of *i*-PrHgCl with 1,4-naphthoquinone in benzene[a]



+ *i*-PrHgCl + [ ] $\xrightarrow{h\upsilon}$ **20** + **21** + **22**

molar equivalents	solvent	% yield[b]		
NaI[KI]:$K_2S_2O_8$[$(NH_4)_2S_2O_8$]:Dabco	(time, h)	**20**	**21**	**22**
0 : 0 : 0	Me_2SO (26)	9	0	0
[4] : 0 : 0	Me_2SO (22)	17	2	tr
[4] : 2 : 0	Me_2SO (15)	46	tr	13
[4] : 2 : 4	Me_2SO (15)	50	0	12
0 : 0 : 0	PhH (24)	44	38	tr
4 : 0 : 0	PhH (24)	19	35	0
4 : 4 : 0	PhH (23)	14	32	0
0 : 0 : 0	PhH (23)[c]	14	46	0
0 : [2] : 0	PhH (23)	24	58	0
0 : 0 : 4	PhH (21)	tr	tr	0
4 : 4 : 4	PhH (23)	30[d]	0	0

[a]Reaction of 0.5 mmol of 1,4-naphthoquinone with 4 equiv of *i*-PrHgCl in 10 ml of Me_2SO or 12 ml of benzene with 275-W GE sunlamp irradiation at ~40 °C.

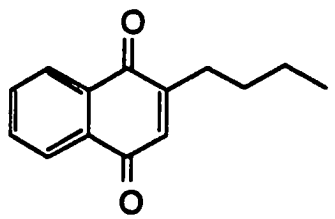
[b]By GC yield with toluene as an internal standard.

[c]4 Vol% AcOH added.

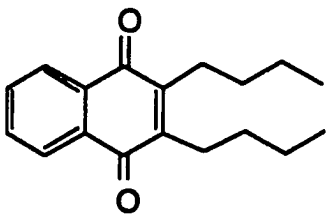
[d]61% of 1,4-Naphthoquinone recovered.

In the presence of proton donors the reductive alkylation is favored, but the reactions do not lead exclusively to **21**. Addition of Dabco for oxidative alkylation lowers the yield and only the combination of NaI(4)/$K_2S_2O_8$(4)/Dabco(4) produces exclusively **20** in 30% yield.

Photolysis of *n*-BuHgCl and 1,4-naphthoquinone in Me_2SO gives only 4% of **23**. By introducing KI or KI/$K_2S_2O_8$, the yields are improved, but the dialkylation product **24** is produced(Table IX).



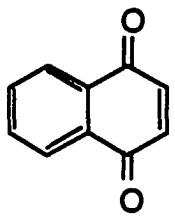
23



24

In benzene solvent, 1,4-naphthoquinone is the major product recovered under all conditions examined. The low yields of alkylation products presumably result because of the low reactivity of *n*-BuHgCl towards the educt radicals.

Table IX. Photostimulated reactions of *n*-BuHgCl with 1,4-naphthoquinone in Me_2SO[a]



+ *n*-BuHgCl + [ ] $\xrightarrow{h\upsilon}$ **23** + **24**

molar equivalents	time (h)	% yield[b]	
KI : $K_2S_2O_8$		**23**	**24**
0 : 0	22	4	0
4 : 0	22	30	6[c]
4 : 2	22	49	25[c]

[a]Reaction of 0.5 mmol of 1,4-naphthoquinone with 4 equiv of *t*-BuHgCl in 10 ml of Me_2SO with 275-W GE sunlamp irradiation at ~40 °C.

[b]GC yield with toluene as an internal standard.

[c]1,4-Naphthoquinone recovered (3 - 8%).

5. Photostimulated reactions of alkylmercury chlorides with acyclic 1,4-enediones

In Section 2 it was reported that enolyl-type radicals formed from *N*-methylmaleimide were readily converted to the saturated alkylation product in the presence of RHgCl/I^- or RHgCl/$I^-/S_2O_8^{2-}$ in Me_2SO. I have also discussed that enolyl-type radicals formed from *N*-methylmaleimide can be coerced to give the oxidative alkylation product in the presence of a base such as Dabco via the formation of a powerful reducing radical anion.

Photolysis of RHgCl (R = *t*-Bu, *i*-Pr, *n*-Bu) in the presence of diethyl maleate, diethyl fumarate, (*E*)-1,2-dibenzoylethylene, or ethyl (*E*)-3-benzoylacrylate gives low yields of the monoalkylation products, even when the reaction is continued until all the substrate is consumed (Table X). However, in the presence of I^- or $I^-/S_2O_8^{2-}$ the products of reductive alkylation are formed in excellent yields with R = *t*-Bu or *i*-Pr. Again, the use of $I^-/S_2O_8^{2-}$ leads to a fast rate of initiation (Scheme 6), and iodide ion promotion involves an increased rate of photoinitiation from ligand exchange and complexation leading to the more labile *t*-BuHgI and *t*-BuHgI_2^-. Reduction of the enolyl radical is believed to involve $RHgI_2^-$ because the effectiveness of I^- depends on the structure of R• (Table XI and XII). The results in Tables XI and XII indicate that the rate of eq. 21 increases from R = *n*-Bu to *i*-Pr to *t*-Bu, i.e. with the stability of the incipient alkyl radical.

Table X. Yields of reductive alkylation products from diethyl maleate (M), diethyl fumarate (F), (*E*)-PhCOCH=CHCOPh (DBE), and (*E*)-PhCOCH=CHCO$_2$Et (B) in Me$_2$SO[a]

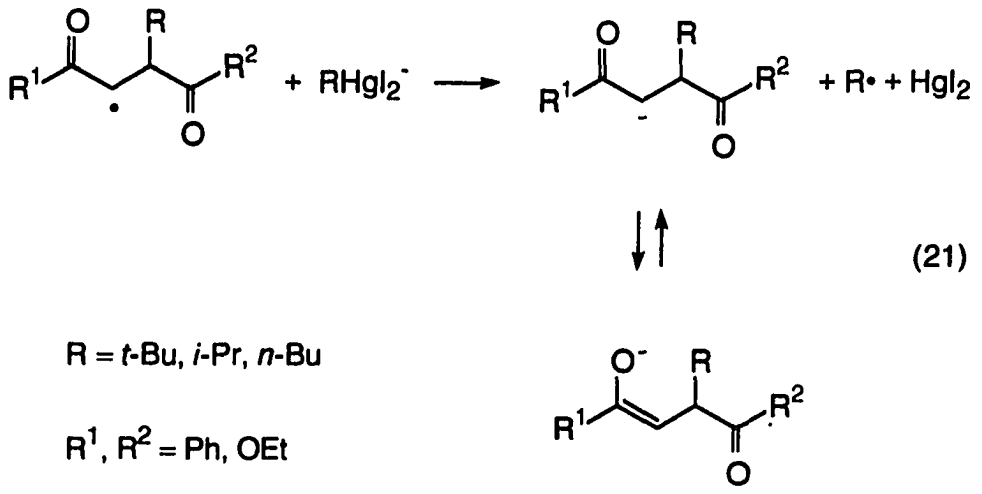
$$R^1C(O)CH{=}CHC(O)R^2 + RHgCl \xrightarrow{h\upsilon} R^1C(O)CH(R)CH_2C(O)R^2$$

R^1, R^2 = OEt, Ph; R = *t*-Bu, *i*-Pr, *n*-Bu

substrate	% yield/R[b] (time)		
	t-Bu	*i*-Pr	*n*-Bu
M	37 (20 h)	43 (18 h)	tr (24 h)
F	39 (14 h)	26 (23 h)	tr (24 h)
DBE	10 (24 h)	9 (45 h)	8 (24 h)
B	6 (24 h)	6 (24 h)	tr (24 h)

[a]Photolysis of 0.5 mmol of substrate with 2.0 mmol of *t*-BuHgCl in 10 ml of Me$_2$SO at ~40 °C.

[b]GC yield with toluene as an internal standard for EtO$_2$CCHRCH$_2$CO$_2$Et, PhCOCH(R)CH$_2$COPh, and PhCOCH$_2$CH(R)CO$_2$Et after aqueous Na$_2$S$_2$O$_3$ work up and ether extraction.



(21)

The yields of Table XI decrease from R = *t*-Bu to R = *n*-Bu. This sequence has been previously observed in other chain reactions of alkylmercurials where competition studies have shown that the rates of S_H2 substitution at Hg(II), e.g. eq. 14 (page 16), or the rate of electron transfer to RHgX, e.g. eq. 15 (page 17), are controlled by the stability of the incipient alkyl radicals.[28] Photostimulated reactions of 1,4-enediones can be controlled by using the proper combination of alkylmercury halides, I^-, $I^-/S_2O_8^{2-}$, and Dabco (Scheme 14). Table XII shows the effect of base (Dabco) in reactions of RHgCl with 1,4-enediones where competition between proton loss and electron transfer (eq. 22 or 23 in Scheme 14) can occur. With maleate or fumarate esters, *t*-BuHgCl/Dabco leads only to the saturated alkylation product. In this case, proton loss to Dabco is unable to compete with eq. 22.

Table XI. Yields of reductive alkylation products from diethyl maleate (M), diethyl fumarate (F), (*E*)-PhCOCH=CHCOPh (DBE), and (*E*)-PhCOCH=CHCO$_2$Et (B) observed in reactions with RHgCl (4 equiv) and KI (4equiv) in Me$_2$SO[a]

$$R^1C(O)CH{=}CHC(O)R^2 + RHgCl + KI + [\ ] \xrightarrow{h\upsilon} R^1C(O)CH(R)CH_2C(O)R^2$$

R^1, R^2 = OEt, Ph

R = *t*-Bu, *i*-Pr, *n*-Bu

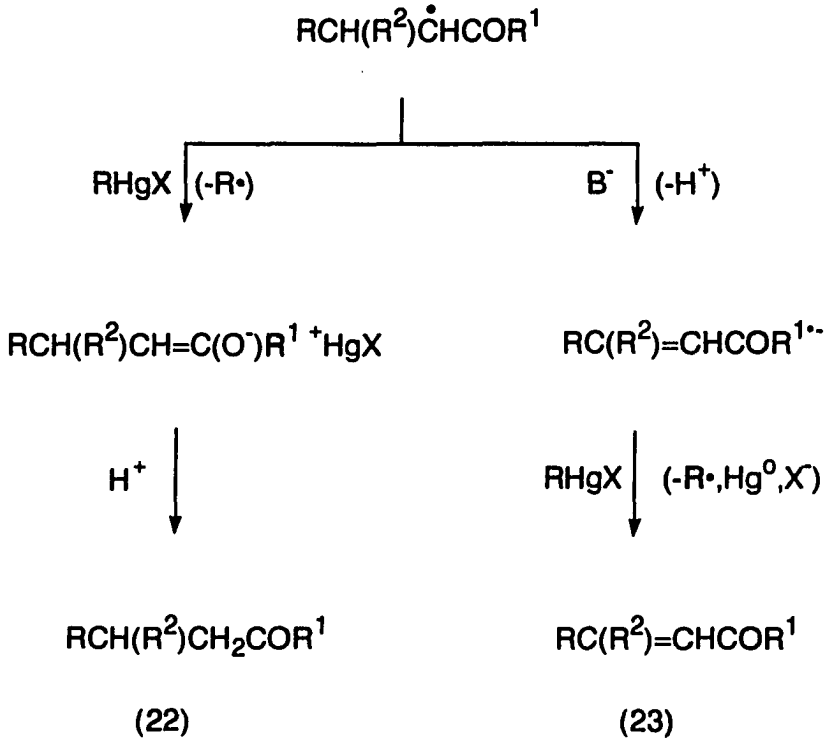
substrate	$K_2S_2O_8$	% yield/R (time, h)[b]		
		t-Bu	*i*-Pr	*n*-Bu
M	-	100 (3)	25 (3.5)	41 (6)
M	1.2 equiv	87 (13)	82 (3)	41 (6)
F	-	52 (3)	83 (3)	46 (4)
F	1.2 equiv	62 (3)	100 (3)	38 (4)
DBE	-	18 (4)	41 (8)	8 (24)
DBE	4.0 equiv	76 (17)	64 (8)	29 (24)
B	-	55 (8)[c]	23 (14)[c]	17 (24)[c]
B	2.0 equiv	63 (8)[c]	52 (14)[c]	25 (24)[c]

[a]Photolysis of 0.5 mmol of substrate in 10 ml of Me$_2$SO for 3 - 24 hours at ~40 °C.

[b]See b, Table X.

[c]Also formed PHCOCH(R)CH$_2$CO$_2$Et, ~8% for R = *t*-Bu, 16 - 22% for R = *i*-Pr, 7% for *n*-Bu.

Scheme 14



(22) (23)

R = alkyl; R^1 = alkyl, aryl, alkoxy; R^2 = H, R^1CO

The presence of Dabco does not necessarily lead to the unsaturated alkylation product since for each enolyl radical there will be a competition between reactions 22 and 23. However, with R = *i*-Pr such competition occurs and the unsaturated alkylation product is formed in a yield which increases with the Dabco concentration. The saturated product is still the exclusive product with Dabco/I^- or Dabco/I^-/$S_2O_8^{2-}$.

Table XII. Photostimulated alkylation reactions of RHgCl in the presence of Dabco with diethyl maleate (M), diethyl fumatate (F), and (*E*)-$PhCOCH{=}CHCO_2Et$ (B) in Me_2SO[a]

$$R^1C(O)CH{=}CHC(O)R^2 + RHgCl + [\quad] \xrightarrow{h\upsilon}$$

$$R^1C(O)CH(R)CH_2C(O)R^2 + R^1C(O)C(R){=}CHC(O)R^2$$

R^1, R^2 = OEt, Ph; R = *t*-Bu, *i*-Pr, *n*-Bu

substrate (R)	molar equivalents	% yield	
	RHgCl:Dabco:KI:$K_2S_2O_8$	sat.[b]	unsat.[c]
M (*t*-Bu)	4 : 4 : 0 : 0	43 (65)[d]	0 (0)[d]
F (*t*-Bu)	4 : 4 : 0 : 0	37	0
F (*t*-Bu)	4 : 4 : 4 : 0	87	0
M (*i*-Pr)	4 : 4 : 0 : 0	11	30
F (*i*-Pr)	4 : 4 : 0 : 0	36	58
M (*i*-Pr)	3 : 10 : 0 : 0	9	57
F (*i*-Pr)	2 : 8 : 0 : 0	12	72[e]
M (*i*-Pr)	3 : 5 : 3 : 0	51	0
M (*i*-Pr)	3 : 5 : 3 : 3	89	0

[a]0.5Mmol of substrate in 10 ml of Me_2SO irradiated at 35 - 40 °C for 24 ± 4 h in the absence of KI, 6 ± 1 h in the presence.

[b]GC yield of $EtO_2CH(R)CH_2CO_2Et$ or $PhCOCH_2CH(R)CO_2Et$.

[c]GC yield of $EtO_2CC(R){=}CHCO_2Et$ or $PhCOCH{=}C(R)CO_2Et$.

[d]In benzene.

[e]35 : 1 mixture of steroisomers by GC and ^1H NMR.

Table XII (continued)

substrate (R)	molar equivalents	% yield	
	RHgCl:Dabco:KI:$K_2S_2O_8$	sat.[b]	unsat.[c]
M (*n*-Bu)	3 : 5 : 0 : 0	0	32[f]
F (*n*-Bu)	4 : 8 : 0 : 0	0	44[g]
M (*n*-Bu)	3 : 5 : 3 : 0	tr	42[g]
M (*n*-Bu)	3 : 5 : 3 : 3	~3	41[f]
B (*t*-Bu)	4 : 4 : 4 : 0	76[h]	12[i]
B (*t*-Bu)	4 : 4 : 4 : 2	61[h]	24[i]
B (*i*-Pr)	4 : 4 : 0 : 0	8[j]	11
B (*i*-Pr)	3 : 10 : 3 : 0	21[h]	18

[f]25 - 30% of substrate recovered.

[g]10 - 12% of substrate recovered.

[h]9% of PhCOCH(R)CH_2CO_2Et from GC and ^{1}H NMR.

[i]2 - 4% of PhCOC(R)=$CHCO_2$Et from GC and ^{1}H NMR.

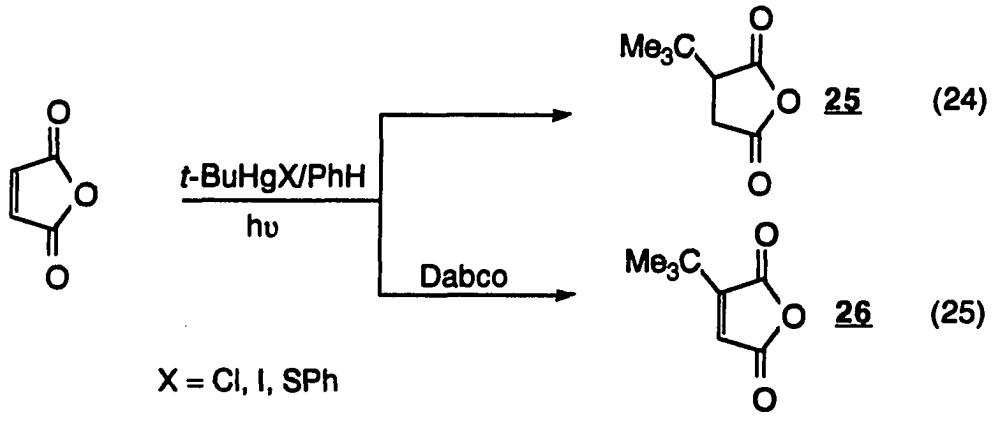
[j]16% of PhCOCH(R)CH_2CO_2Et from GC and ^{1}H NMR.

Finally, with R = *n*-Bu the unsaturated product greatly predominates in the presence of Dabco with or without I^-. The results cleanly demonstrate that the competition between proton loss to Dabco from the enolyl radical and electron transfer from $RHgI_2^-$ to the enolyl radical increasingly favors the electron transfer process as R is changed from *n*-Bu (only proton loss) to *i*-Pr to *t*-Bu (only electron transfer).

6. Photostimulated reactions of alkylmercurials with maleic anhydride

The previous Scheme 14 could work for maleic anhydride also. Various

attempts at reductive and oxidative alkylation fails in Me_2SO, possibly because of the ionic reactivity of maleic anhydride in Me_2SO. However, in a nonpolar solvent such as benzene, the *tert*-butylation of maleic anhydride by techniques described in Scheme 14 allows either the reductive or oxidative alkylation product to be formed exclusively and in moderate yield. (Table XIII).



By adding an excess of *t*-BuI (20 equiv) to a mixture of maleic anhydride (1)/*t*-BuHgCl (4)/PhH, the yield for reductive alkylation is improved to 54% (24 h) presumably because of in situ formation of *t*-BuHgI (Scheme 15)

Scheme 15

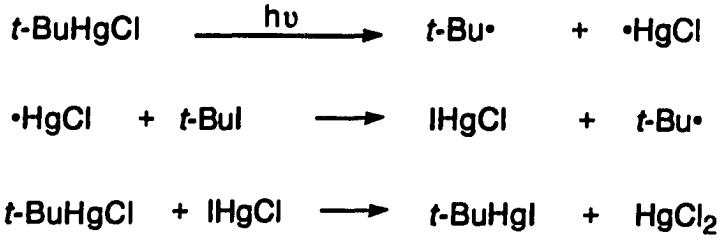
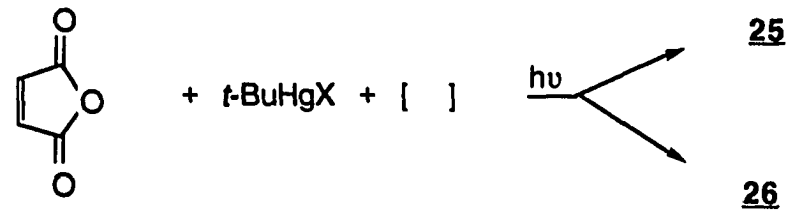


Table XIII. Photostimulated reactions of maleic anhydride in benzene[a]



X	molar equivalents	time (h)	yield (%)[b]	
	t-BuHgX:KI:Dabco		25	26
Cl	4 : 0 : 0	25	36	tr
Cl	4 : 4 : 0	20	46	tr
SPh	2 : 0 : 0	5	35	-
I	2 : 0 : 0	4	60	-
Cl	8 : 0 : 4	17	-	31

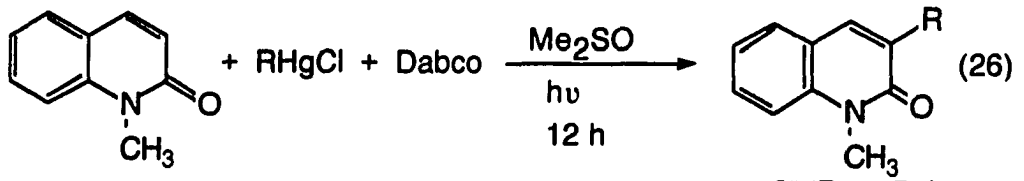
[a]0.5mmol of substrate in 10 ml of benzene irradiated with a 275-W GE sunlamp at 35 - 40 °C.

[b]GC yield with toluene as an internal standard after work up and extraction.

Consideration of the relative reactivity of *t*-BuHgI, *t*-BuHgCl, and *t*-BuHgSPh towards enolyl radical will be discussed in detail in Section 9.

7. Oxidative alkylations of 1-methyl-2(1*H*)-quinolinone and perinaphthenone

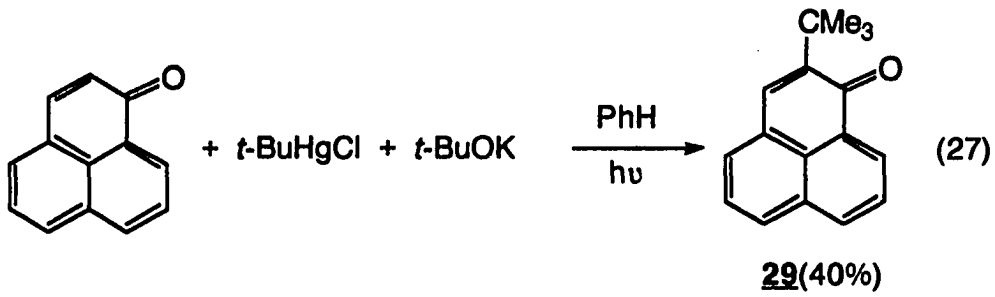
1-Methyl-2(1*H*)-quinolinone, similar to coumarin, react with aikyi radicals by α-attack to generate the benzylic radical, which reacts slowly or not at all with RHgCl. Again, addition of Dabco (4 equiv) to 1-methyl-2(1*H*)-quinolinone (1)/RHgCl (4) in Me_2SO gives rise to oxidative alkylation to form α-alkylated product in moderate yield (R = *t*-Bu, 40%; R = *i*-Pr, 30%).



27(R = *t*-Bu)

28(R = *i*-Pr)

Perinaphthenone fails to give the reductive or oxidative alkylation products under most conditions and perinaphthenone is recovered as the major reaction product. However, by using a strong base such as *t*-BuOK, oxidative alkylation is achieved. Perinaphthenone (1)/*t*-BuHgCl (4)/*t*-BuOK (4)/hυ in Me_2SO (20 h) produces 28% of oxidative alkyltion product **29** accompanied by by-products while perinaphthenone (1)/*t*-BuHgCl (4)/Dabco (4)/hυ in Me_2SO (43 h) produces only 3% of **29**. The use of benzene as a solvent under the similar conditions (perinaphthenone (1)/*t*-BuHgCl (4)/*t*-BuOK (4)/hυ/20 h) improves the yield of **29** to 40% (reaction 27).



(27)

29(40%)

8. Further examples of reductive alkylations of α,β-unsaturated carbonyls via free radical chain reactions

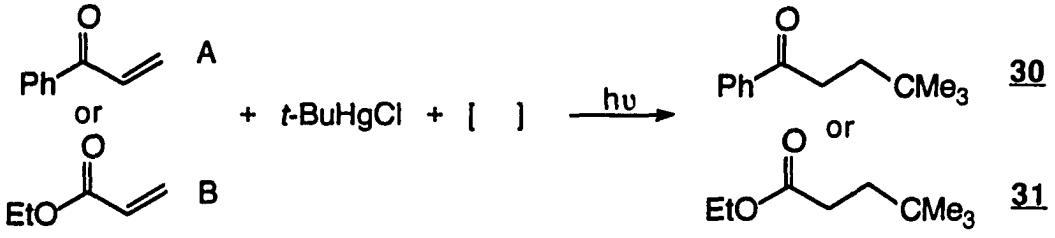
Photostimulated chain reactions of alkylmercury chlorides with α,β-unsaturated carbonyls have been described by Russell et al.[35,36] The reactions are dramatically promoted by the presence of iodide salts. As discussed in previous sections, $I^-/S_2O_8^{2-}$ also promotes reductive alkylations. More examples of the reductive alkylation of α,β-unsaturated carbonyls are reported in this section.

For phenyl vinyl ketone, ethyl acrylate, or diethyl ethylidenemalonate, the addition of I^- or $I^-/S_2O_8^{2-}$ to the reaction mixture also promotes the reaction to produce higher yields of the reductive alkylation product while the addition of Dabco fails to produce the oxidative alkylation presumably because the educt radical has no acidic proton to transfer to the Dabco (Tables XIV and XV).

In case of diethyl benzalmalonate and *N*-acryloylaniline, the yields are also improved by using the I^- or $I^-/S_2O_8^{2-}$ system. In addition, interestingly, if we use *t*-BuHgI instead of *t*-BuHgCl, the yields are improved in both cases but are still lower than the yields with the *t*-BuHgCl/KI combination. Furthermore, the mixture of *t*-BuHgI/KI seems better than *t*-BuHgCl/KI for reductive alkylation

(Tables XVI and XVII). The differentiation of the reactivity of each system will be discussed in detail in Section 9.

Table XIV. Photostimulated reactions of phenyk vinyl ketone and ethyl acrylate in Me_2SO[a]



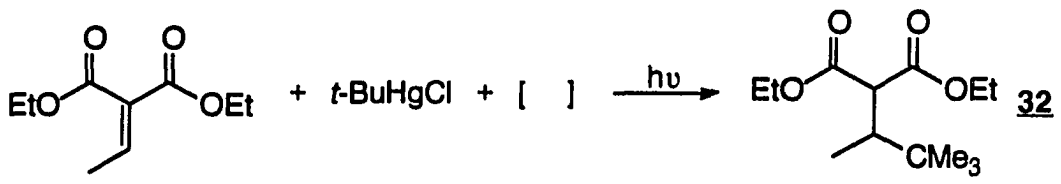
substrate	molar equivalents	time	% yield[b,c]
	t-BuHgCl:KI:$K_2S_2O_8$:Dabco		(product)
A	4 : 0 : 0 : 0	18 h	29 (**30**)
A	4 : 8[d]: 0 : 0	18 h	57 (**30**)
A	4 : 8[d]: 2 : 0	18 h	86 (**30**)
A	4 : 0 : 0 : 4	13 h	11 (**30**)
B	4 : 4 : 0 : 0	10 min	78 (**31**)
B	4 : 0 : 0 : 4	20 h	8 (**31**)

[a]0.5 Mmol of substrate in 10 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]GC yield with toluene as an internal standard.

[c]2 Telomers formed as by-products. [d]NaI used instead of KI.

Table XV. Photostimulated reactions of diethyl ethylidenemalonate in Me_2SO[a]



32

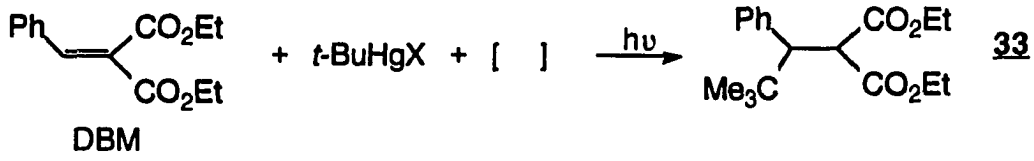
molar equivalents t-BuHgCl:KI:$K_2S_2O_8$:Dabco	time (h)	% yield of 32
4 : 0 : 0 : 0	28	46[c]
4 : 8 : 0 : 0	19.5	50
4 : 8 : 2 : 0	19.5	64
4 : 0 : 0 : 6	28	10[c]
4 : 4 : 0 : 4	6.5	24

[a]0.5 Mmol of substrate in 10 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]GC yield with toluene as an internal standard.

[c]Starting substrate recovered (11 - 15%).

Table XVI. Photostimulated reactions of diethyl benzalmalonate (DBM) in Me_2SO[a]



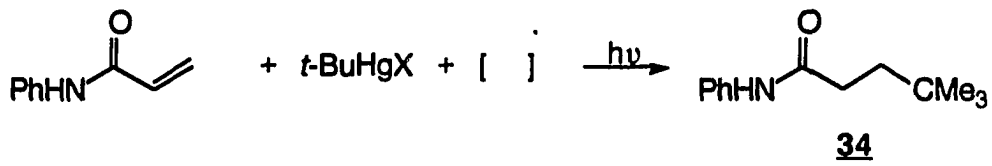
DBM

X	molar equivalents	time (h)	% yield[b]	
	t-BuHgX:KI:$K_2S_2O_8$		DBM	33
Cl	4 : 0 : 0	43	72	4
I	4 : 0 : 0	43	24	44
Cl	6 : 6 : 0	45	10	61
I	4 : 4 : 0	19	4	70
Cl	4 : 4 : 2	19	tr	40

[a]0.5 Mmol of substrate in 10 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]GC yield with toluene as an internal standard.

Table XVII. Photostimulated reactions of *N*-acryloylaniline in Me_2SO[a]



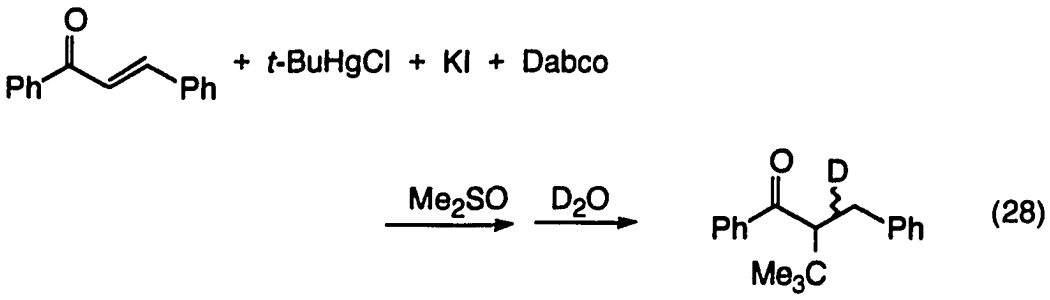
34

X	molar equivalents *t*-BuHgX:KI:Dabco	time (h)	% yield of **34**[b]
Cl	6 : 0 : 0	31	12
I	6 : 0 : 0	22	68
Cl	6 : 6 : 0	22	92
Cl	6 : 0 : 6	48	5
I	6 : 0 : 6	36	58
Cl	6 : 6 : 6	36	89

[a]0.5 Mmol of substrate in 10 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]GC yield with toluene as an internal standard.

The photostimulated reaction of chalcone with *t*-BuHgX produces the α-*tert*-butylated saturated product under all conditions even in the presence of a base. Chalcone reacts with *tert*-butyl radical by α-attack to generate the benzylic radical, which seems to react slowly with *t*-BuHgX. A chain reaction for oxidative alkylation is not successful even though the adduct radical has an acidic α-hydrogen atom. Workup with D_2O gives deutrated product by GCMS (eq. 28 and Figure 1).



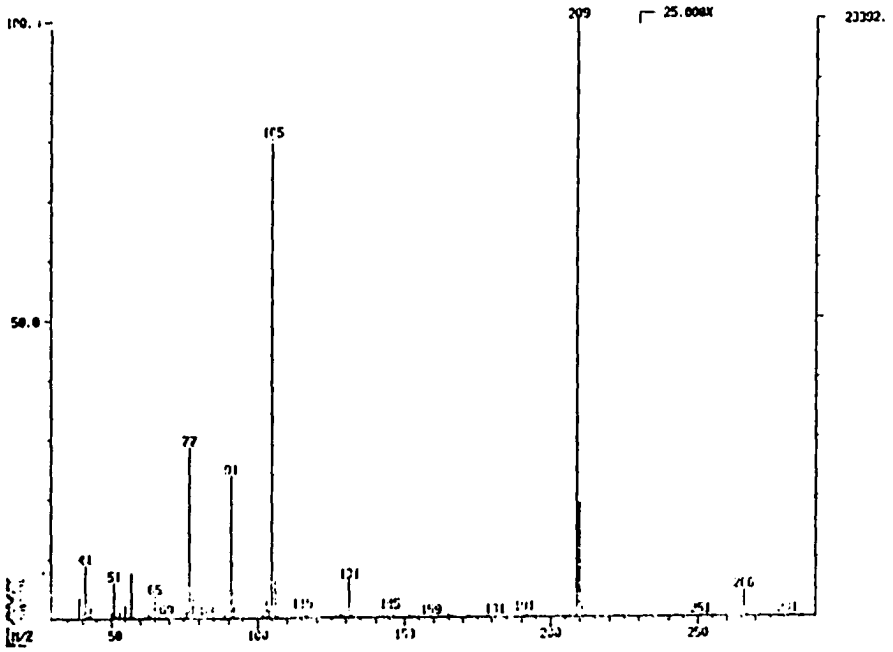
(28)

Loss of proton from the adduct radical seems may occur but perhaps it does not give the delocalized radical anion. Possibly because of steric and electronic effects a distonic radical anion is formed as shown in Scheme 16. The results are summarized in Table XVIII. In general, again, yields increase in the order of *t*-BuHgCl < *t*-BuHgI < *t*-BuHgCl/I^- ≤ *t*-BuHgI/I^-. The reactivity difference of these systems will be discussed in Section 9.

Chalcone shows essentially no reaction with *t*-BuHgCl/hυ. However, by introducing the anion such as HO^- or *t*-BuO^- the reductive alkylation product is observed.

1) H_2O

Work up.



2) D_2O

Work Up.

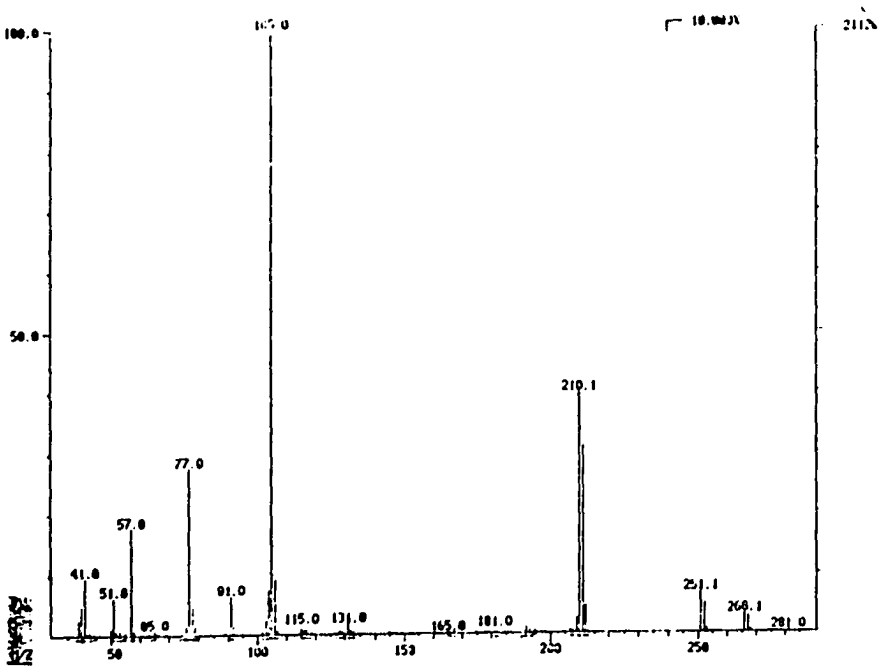
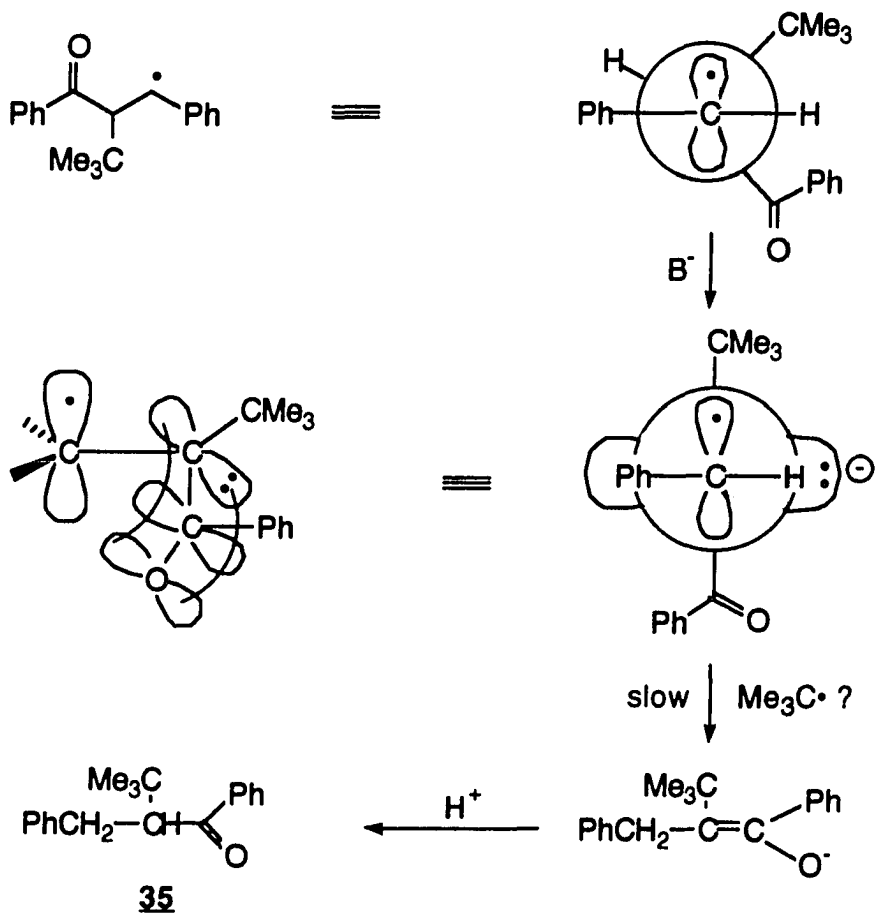


Fig. 1. Mass spectra of deutration experiments of chalcone reactions (MW of PhCOCH(Bu-*t*)CH_2Ph = 266).

Scheme 16

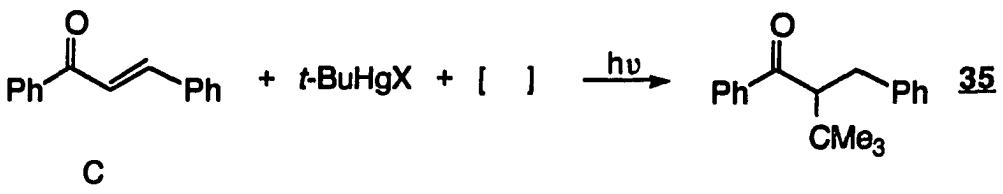


35

% $PhCH_2CH(Bu\text{-}t)COPh$

KI/$K_2S_2O_8$/Me_2SO	KI/Me_2SO	KO*t*-Bu/Me_2SO	KOH/Me_2SO
60	36	32	23
	t-BuOK/PhH	KOH/PhH	
	52	41	

Table XVIII. Photostimulated reactions of chalcone (C) with t-BuHgX[a]



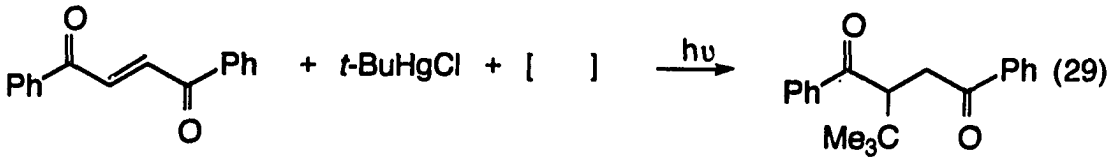
C

X	molar equivalents	solvent	% yield[b]	
	t-BuHgX:KI:$K_2S_2O_8$:Dabco	(time, h)	C	35
Cl	4 : 0 : 0 : 0	Me_2SO (22)	>90	-
I	4 : 0 : 0 : 0	Me_2SO (24)	23	27
I	4 : 0 : 0 : 0	PhH (24)	12	35
Cl	4 : 4 : 0 : 0	Me_2SO (21)	-	36
I	4 : 4 : 0 : 0	Me_2SO (21)	-	44
Cl	4 : 4 : 2 : 0	Me_2SO (22)	-	60
Cl	4 : 0 : 0 : 4	Me_2SO (22)	-	16
I	4 : 0 : 0 : 4	Me_2SO (26)	tr	18
I	4 : 0 : 0 : 4	PhH (24)	12	35
Cl	4 : 4 : 0 : 4	Me_2SO (20)	-	30
Cl	4 : 4 : 0 : 4	PhH (30)	-	39

[a]0.5 Mmol or 0.25 mmol of chalcone in 10 ml or 5 ml of solvent irradiated with a 275-W GE sunlamp at ~40 °C.

[b]GC yield with toluene as an internal standard or ^1H NMR with toluene as an internal standard if starting chalcone left.

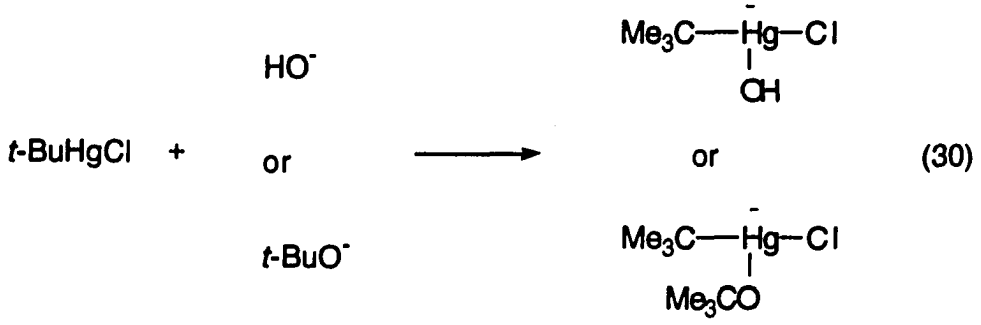
The reactions of 0.5 mmol of chalcone with 4 equiv of *t*-BuHgCl/4 equiv of an anion does not show real difference with the structure of the anion as shown above (page 53). A similar result is observed for the photostimulated reaction of dibenzoylethylene with *t*-BuHgCl.



(29)

DBE (1)/*t*-BuHgCl (4) in Me_2SO for 24 h	10%
DBE (1)/*t*-BuHgCl (4)/KOH (4) in Me_2SO for 2.5 h	32%
DBE (1)/*t*-BuHgCl (4)/*t*-BuOK (2) in PhH for 4 h	52%

The anion in solution is believed to form ate complexes with the mercurial and promote the reaction similar to I^-/Me_2SO.

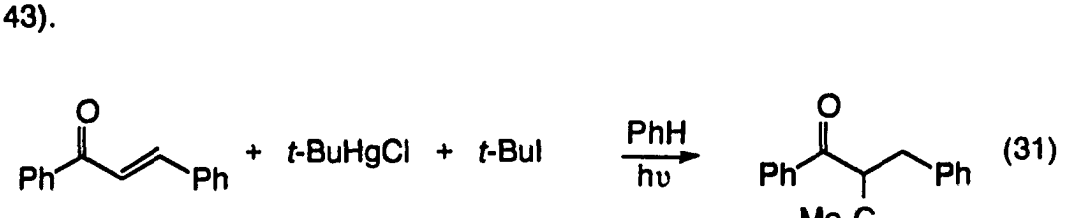


(30)

The photochemical reaction of *t*-BuHgCl (4 equiv)/KI (4) with chalcone to form $PHCH_2CH(COPh)CMe_3$ is not promoted by PTSA (4) and yields of the reductive

β-alkylation product is reduced (18 h, 12%) by the presence of PTSA, presumably because the adduct radical does not contain an easily protonated radical center.

Addition of an excess amount of *t*-BuI (20 equiv) into chalcone (1)/*t*-BuHgCl (4) in benzene solution improves the yield of the reductive alkylation product (56%, 31 h) from chalcone (eq. 31) similar to the maleic anhydride reaction because of in situ formation of *t*-BuHgI as described in Scheme 15 (page 43).



(31)

i-PrHgCl or *n*-BuHgCl failed to react with chalcone in Me_2SO even in the presence of added anions. The mixture, chalcone (1)/*i*-PrHgI (4)/Dabco (4) in benzene solution produces only 21% of the saturated alkylated product after 44 hours with chalcone (26%) recovered. In all reactions with *n*-BuHgCl, chalcone was recovered as the major product.

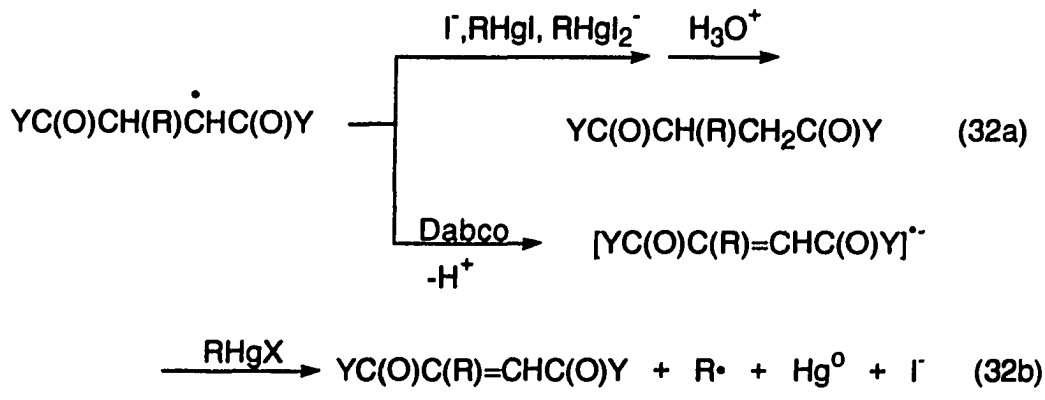
9. Study of effect of iodide ion on the free radical alkylation of enones by alkylmercury halides

The conversion of α,β-unsaturated carbonyl compounds into β-alkylated derivatives in a free radical chain reaction with alkylmercury chlorides is dramatically promoted by the presence of iodide salts. It has been suggested that iodide functions by formation of the ate-complex ($RHgI_2^-$) which readily reduces

the adduct radical. However, the conversion of the enolyl radical to the enolate product could involve free I^- or RHgI. The thrust of this section is to demonstrate how these possibilities can be distinguished. The results demonstrate that free iodide ion is ineffective in the enolyl to enolate conversion and that *t*-BuHgX/KI is more effective than *t*-BuHgI alone. To separate the effects due to I^-, RHgI, and $RHgX_2^-$, we have studied the competition between reactions 32a and 32b for enolyl radicals derived from 1,4-enediones. (reaction 32b involves the loss of a proton from the enolyl radical to form the 1,4-semidione radical anion which transfers an electron to RHgCl).

In a reaction incorporating both I^- and Dabco, product formation will involve competing bimolecular reactions of a common enolyl intermediate, Scheme 17. As formulated in Scheme 17, the products will be controlled by the competing reactions of the enolyl radical. By holding the concentration of Dabco

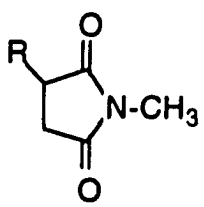
Scheme 17



constant it is possible to dissect the variables which control the rate of the rate of the reduction of the enolyl radical to the enolate product.

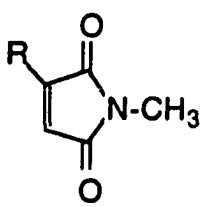
By using diethyl fumarate as the substrate and varying the nature of the alkyl group in RHgCl/I$^-$ systems, it is clear that the iodide promotion is a function of the alkyl group (Table XIX). This requires that the competition between reduction to the enolate and the loss of a proton involves a trapping agent containing the alkyl group, i.e. RHgI or $RHgI_2^-$. [It is assumed that effect of the structure of R upon the reactivity of the enolyl radical can be ignored].

The question now remains whether RHgI or $RHgI_2^-$ is responsible for the conversion of the enolyl radical to the saturated alkylation product since in many systems *t*-BuHgI is about as effective as *t*-BuHgCl/I$^-$ in forming the product.[38] Table XX presents data with *N*-methylmaleimide which demonstrate that *t*-BuHgCl/KI or *t*-BuHgI/KI systems are more effective than *t*-BuHgI alone in the conversion of enolyl radicals to the saturated alkylation product. Again, competition with proton abstraction by Dabco was employed. With *t*-BuHgCl/Dabco the unsaturated product **10** is now formed in up to 95% yield (diethyl fumarate gave only the saturated product) while t-BuHgI/Dabco (4 equiv each) gives a mixture of **9** (35%) and **10** (53%). However, a mixture of *t*-BuHgCl



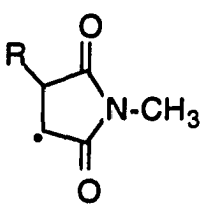
9(R = *t*-Bu)

11(R = *i*-Pr)



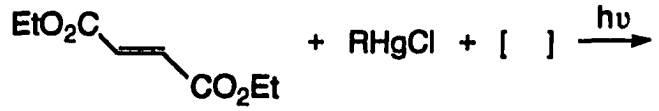
10(R = *t*-Bu)

12(R = *i*-Pr)



36(R = *t*-Bu)

Table XIX. Photostimulated reactions of RHgCl with diethyl fumarate in the presence of KI or Dabco in Me_2SO[a]



$EtO_2CCH(R)CH_2CO_2Et$(sat.) + $EtO_2CC(R)=CHCO_2Et$(unsat.)

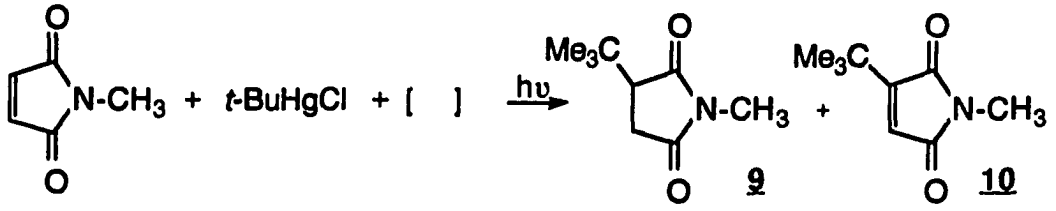
R	time, h	molar equivalents	% yield[b]	
		RHgCl:KI:Dabco:$K_2S_2O_8$	sat.	unsat.[c]
t-Bu	14	4:0:0:0	39	0
t-Bu	3	4:4:0:0	52	0
t-Bu	3	4:4:0:2	62	0
t-Bu	10	4:4:4:0	87	0
t-Bu	24	4:0:4:0	37	0
i-Pr	22	4:0:0:0	26	0
i-Pr	3	4:4:0:0	83	0
i-Pr	3	4:4:0:2	100	0
i-Pr	11	4:4:4:0	89	0
i-Pr	23	4:0:4:0	36	58
i-Pr	23	2:0:8:0	12	72
n-Bu	4	4:4:0:0	46	0
n-Bu	4	4:4:0:2	38	0
n-Bu	10	4:4:4:0	5	53
n-Bu	24	4:0:8:0	0	44

[a]2.0mmol of RHgCl in 10 ml of Me_2SO irradiated at 35 - 40 °C with a 275-W GE sunlamp.

[b]By GC with an internal standard.

[c]One stereoisomer with δ = 6.4 (*i*-Pr), 6.7 (*n*-Bu) for the vinyl hydrogen atoms. The (*Z*) stereochemistry can be assigned for R = *i*-Pr.

Table XX. Alkylation of *N*-methylmaleimide by *t*-BuHgX in the presence of KI and Dabco in Me_2SO[a]

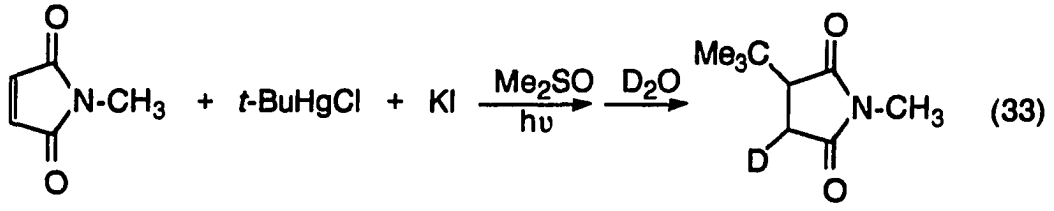


X	molar equivalents	% yield (time)[b]	
	t-BuHgCl:KI:Dabco:$K_2S_2O_8$	9	10
Cl	4 : 0 : 0 : 0	37 (4 h)	0
Cl	4 : 4 : 0 : 2	99 (20 min)	0
Cl	4 : 0 : 8 : 0	tr	95 (6 h)
Cl	4 : 8 : 4 : 0	99 (20 min)	0
I	4 : 0 : 0 : 0	95 (4 h)	0
I	4 : 0 : 4 : 0	35 (5 h)	53 (5 h)
I	4 : 8 : 4 : 0	58 (10 min)	0

[a]2.0mmol of RHgCl in 10 ml of Me_2SO irradiated at 35 - 40 °C with a 275-W GE sunlamp.

[b]By GC with an internal standard.

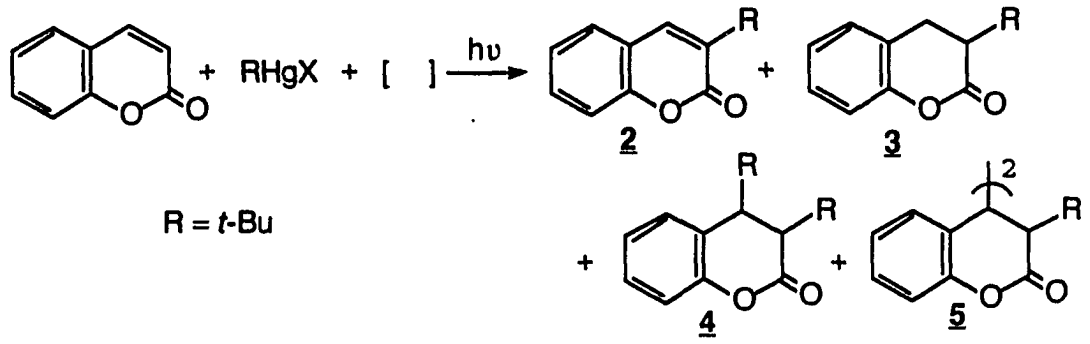
(4)/KI (8)/Dabco (4) gives **9** in a yield of 99%. Obviously *t*-BuHgCl/2KI is more effective than *t*-BuHgI in converting **36** to the enolate product. Work up with D_2O gives >70% of monodeutrated **9** consistent with the formation of an enolate salt.



(33)

A similar tendency is observed for the coumarin reactions are summarized in Table XXI. For reductive alkylations, yields are increased relative to *t*-BuHgCl by use of *t*-BuHgI, *t*-BuHgCl/KI, or *t*-BuHgI/KI. The effectiveness of each system in forming the saturated alkylation product is more clear when Dabco is employed and a competitive oxidative alkylation observed. The least effective reagent for the conversion of an enolyl radical to the saturated product is *t*-BuHgCl which shows mainly unsaturated product **2** (90%) with a ratio of >10 : 1 of unsaturated : saturated. With the more effective reducing systems the ratio of unsaturated: saturated alkylation products decreased [*t*-BuHgCl (>10 : 1) < *t*-BuHgI (5.3 : 1) < *t*-BuHgCl/KI (4 : 1) < *t*-BuHgI/KI (3.8 : 1)]. The relative effectiveness of *t*-BuHgCl vs. *t*-BuHgI is also clearly demonstrated by an ^1H NMR analysis of the reaction with maleic anhydride in benzene-d_6 and, in addition, the effectiveness of *t*-BuHgSPh is between *t*-BuHgCl and *t*-BuHgI (Table XXII and Figure 2). For

Table XXI. Alkylation of coumarin by *t*-BUHgX in the presence of KI and Dabco in Me_2SO[a]



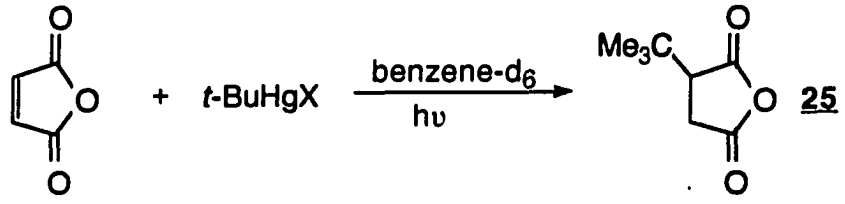
X	molar equivalents t-BuHgX:KI:Dabco	time (h)	% yield[b] 2	3	4	5
Cl	4 : 0 : 0	24	tr	tr	-	-
Cl	4 : 0 : 4	12	90	<9	-	-
I	4 : 0 : 0	20	tr	12	11	14
I	4 : 0 : 4	5	64	12	tr	3
Cl	4 : 8 : 0	6	2	10	14	7
Cl	4 : 4 : 4	5	44	11	tr	3
I	4 : 4 : 4	4	57	15	tr	3

[a]2.0Mmol of RHgCl in 10 ml of Me_2SO irradiated at 35 - 40 °C with a 275-W GE sunlamp.

[b]By GC with toluene as an internal standard.

complete reaction, maleic anhydride with *t*-BuHgI in benzene-d_6 required 95 min while maleic anhydride with *t*-BuHgSPh in benzene-d_6 took 110 min. With *t*-BuHgCl in benzene-d_6, the reaction required >>420 min for completion.

Table XXII. Reaction of Maleic anhydride with *t*-BuHgX[a]



time (min)	% yield (100 - maleic anhydride)[b]		
	t-BuHgCl	*t*-BuHgSPh	*t*-BuHgI
0	0	0	0
30	-	41	-
35	0	-	64
50	-	59	-
65	0	-	94
75	-	84	-
95	0	-	100
110	-	100	-
140	tr	-	-
420	32	-	-
1140	100	-	-
	36[c]	35[c]	60[c]

[a]0.1 Mmol of maleic anhydride with 0.2 mmol of *t*-BuHgX in 1 ml of benzene-d_6 irradiated with a GE sunlamp at ~40 °C.

[b]By NMR with benzene as an internal standard.

[c]By GC with toluene as an internal standard after work up.

Curve A: with *t*-BuHgI (60%)

Curve B: with *t*-BuHgSPh (35%)

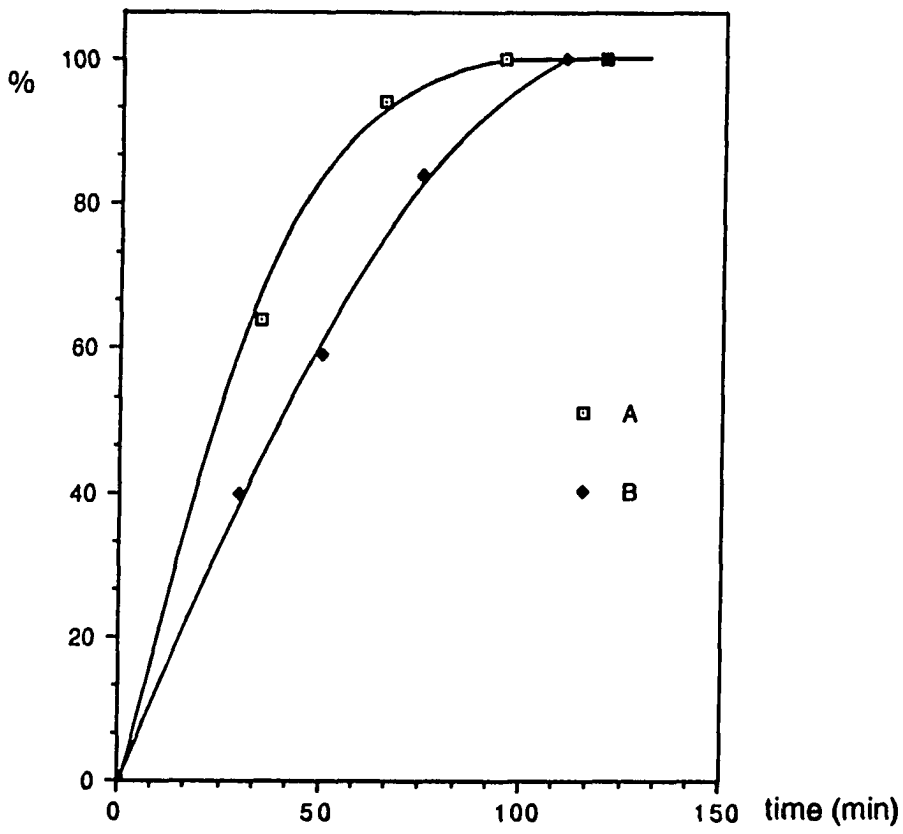


Fig. 2. Reactions of maleic anhydride with t-BuHgX. Values in ( ) are isolated yields of saturated alkylation product.

D. Conclusion

Photostimulated chain reactions of alkylmercury halides with α,β-unsaturated carbonyls or 1,4-enediones occur readily to produce reductive alkylation products in the presence of I^- or $I^-/S_2O_8^{2-}$. With I^- or $I^-/S_2O_8^{2-}$ enolyl radicals can be reduced to the enolate anion and the chain reaction propagated. In the presence of Dabco the intermediate enolyl radical which is formed in the free radical chain reactions of alkylmercury halides with 1,4-enediones can be deprotonated to a radical anion which yields the oxidative alkylation product upon electron transfer to the alkylmercury halide. Reductive and oxidative alkylations compete with each other and reductive alkylations are observed in some cases even in the presence of Dabco depending on the reactivity of the alkylmercury halides and the structure of substrate.

By measuring the competition between reductive and oxidative alkylation, the nature of the iodide ion effect in the conversion of the enolyl radical to the enolate product is revealed. Free iodide ion is ineffective in the enolyl to enolate conversion and the effectiveness for the enolyl to enolate conversion increases in the order of *t*-BuHgI/I^- ≥ *t*-BuHgCl/I^- > *t*-BuHgI > *t*-BuHgCl. The ate complex, *t*-BuHgI_2^- is thus implicated in the reduction of the enolyl radical to the enolyl anion.

E. Experimental Section

1. General consideration

Analytical gas chromatography (GC) was performed on a Varian 3700 gas chromatograph equipped with a Hewlett-Packard 3390A integrator. ^{1}H and ^{13}C NMR spectra were obtaineded with a Nicolet NT300 spectrometer. Chemical shifts were reported in ppm from internal tetramethylsilane (^{1}H NMR) or from $CDCl_3$ (^{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 Digilab FTS-7 FT spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were 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 TLC (silica gel) technique. 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 or dichloromethane).

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 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

n-Butylmercury chloride and isopropylmercury chloride were prepared by literature method[50], and *tert*-butylmercury halides were prepared by modified literature method. They were usually prepared from the Grignard reagents and mercury salts (1 : 1 equiv) in THF. Thus prepared were *n*-butylmercury chloride (mp 127.5 °C)[51], isopropylmercury chloride (mp 163 - 164 °C)[52], *tert*-butylmercury chloride (mp found 110 - 113 °C, literature:[53] mp 123 °C), and *tert*-butylmercury iodide.

a. *tert*-Butylmercury chloride *t*-BuHgCl was prepared from mercuric chloride and *t*-BuLi. A solution containing mercuric chloride (0.18 mol) in dry ether (500 ml) was stirred in an ice bath under nitrogen and *t*-BuLi (0.17 mol, 1.7 M solution in pentane) was added dropwise. After addition, the mixture was stirred for several 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 $MgSO_4$. 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; ^1H 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 *t*-BuLi (0.17 mol, 1.7 M solution in pentane) was added dropwise. After

addition, the mixture was stirred for 2 hours at room temperature. The mixture 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 $MgSO_4$, evaporation, and two recrystallization give the white needles of *t*-BuHgCl.

b. ***tert*-Butylmercury iodide** *t*-BuHgI was prepared by a modified anion exchange method.[54] *t*-BuHgCl (0.03 mol) was mixed with a two-fold excess of potassium iodide in 40 ml of Me_2SO solution and the solution stirred for 2 hours at room temperature. The reaction was quenched by adding 100 ml of water and the mixture extracted with ether (70 ml x 2) and the combined organic extract filtered through a celite-filled cintered glass funnel and washed 3 times with water (100 ml x 3). The solution was dried over $MgSO_4$ and the solvent was evaporated until white crystals precipitated. The solution was filtered immediately. The white crystals turned pale yellow crystals when exposed to the air within a half hour and turned greenish-yellow for several hours.; ^1H NMR ($CDCl_3$) δ 1.42(s, 9H).

4. General procedure for attempted photostimulated reductive alkylations of coumarin

Coumarin (0.5 mmol), *t*-BuHgCl (2.0 mmol), and KI (2.0 mmol), or coumarin (0.5 mmol), *t*-BuHgCl (2.0 mmol), KI (2.0 mmol), and with or without $K_2S_2O_8$ (1.0 mmol) were placed in flame-dried pyrex test tube and 10 ml of deoxygenated Me_2SO was added under nitrogen. With stirring the solution was irradiated with a 275-W sunlamp ca. 25 cm from the reaction test tube for 16 hours. The reaction mixture was then poured into 25 ml of saturated sodium

thiosulfate solution and extracted three times with methylene chloride or ether (15 ml each). The combined organic extract was washed three times with 10% sodium thiosulfate, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and each compound was isolated by flash column chromatography (hexane : ethyl acetate = 96 : 4) and characterized by instrumental analysis. After the work up, trace of 3-*tert*-butylcoumarin (2), 20% of 3-*tert*-butyldihydrocoumarin (3), ~33% of 3,4-di-*tert*-butyldihydrocoumarin (4), and ~40% of 4 isomers of 3,3'-di-*tert*-butyl-4,4'-bidihydrocoumarin (5) were obtained in the presence of KI. In the presence of $KI/K_2S_2O_8$, trace of 3-*tert*-butylcoumarin (2), 19% of 3-*tert*-butyl dihydrocoumarin (3), ~32% of 3,4-di-*tert*-butyl dihydrocoumarin (4), and 42% of 4 isomers of 3,3'-di-*tert*-butyl-4,4'-bidihydrocoumarin (5) were obtained. Of these isomers of 5, only one isomer was isolated. Yields were determined by GC analysis with toluene (0.5 equiv) as an internal standard.

a. **3-*tert*-Butylcoumarin (2)** Compound 2 was isolated as a white solid, mp 82 - 83 °C; ^1H NMR ($CDCl_3$) δ 1.40 (s, 9H), 7.20 - 7.35 (m, 2H), 7.35 - 7.50 (m, 2H), 7.54 (s, 1H); GCMS m/z (relative intensity) 202 (M^+, 45), 187 (100), 160 (85), 144 (11), 133 (17), 115 (31), 103 (4), 91 (17), 77 (10), 57 (5), 51 (15); HRMS m/z cald for $C_{13}H_{14}O_2$ 202.0994, found 202.0991; FTIR ($CDCl_3$) 2964 (m), 1722 (vs), 1705 (s) cm^{-1}.

b. **3-*tert*-Butyldihydrocoumarin (3)** Compound 3 was isolated as a white solid, mp 43 - 45 °C; ^1H NMR ($CDCl_3$) δ 0.95 (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 (relative intensity) 204 (M^+, 11), 148 (100), 91 (20), 57 (85); HRMS

m/z cald for $C_{13}H_{16}O_2$ 204.1150, found 204.1151; FTIR ($CDCl_3$) 2966 (m), 2901 (w), 1765 (s) cm^{-1}.

c. **3,4-Di-*tert*-butyldihydrocoumarin (4)** Compound 4 was identified by GC and GCMS only because of separation problem; GCMS m/z (relative intensity) 260 (M^+, 2), 204 (4), 189 (5), 147 (100), 57 (32).

d. **3,3'-Di-*tert*-butyl-4,4'-bidihydrocoumarin (5)** one isomer of 5 was isolated as a white solid (85% pure, 15% of isomer)with mp >150 °C (melted gradually because of isomer contamination); ^1H NMR ($CDCl_3$) δ 0.86 (s, 18H), 2.77 (s, 2H), 2.92 (s, 2H), 6.20 (dd, 2H, J = 1.2, 7.5 Hz), 6.72 (dt, 2H, J = 1.2, 7.5 Hz), 6.98 (dd, 2H, J = 1.2, 7.5 Hz), 7.12 (dt, 2H, J = 1.2, 7.5 Hz); GCMS m/z (relative intensity) 407 (M^+ + 1, 0.1), 391 (M - Me, 1), 349 (M - *t*-Bu, 4), 293 (2), 203 (24), 147 (100), 57 (19); HRMS m/z cald for $C_{26}H_{31}O_4$ (MH^+) 407.2222, found 407.2213; FTIR ($CDCl_3$) 2962 (m), 1755 (s) cm^{-1}.

5. Procedure for the reaction of coumarin with higher order organocuprate

CuCN (0.7 mmol) was placed in a 25 ml flask and was flushed with nitrogen. THF (10 ml) was introduced and the slurry was cooled to -78 °C. *t*-BuLi (1.75 mmol) was added via syringe and the mixture stirred for 20 min (until complete dissolution of the CuCN). Coumarin (0.5 mmol) in 10 ml of THF was added via syringe. The solution was stirred for 5 hours at -78 °C and allowed to warm to room temperature and poured into aqueous NH_4Cl solution. the reaction mixture was extracted, dried, and concentrated. The product ratio was determined by GC analysis with toluene as an internal standard. The products were 2 (trace), 3 (16%), 4 (14%), and 5 (42%).

6. General procedure for photostimulated oxidative alkylations of coumarin

Coumarin (0.5 mmol), *t*-BuHgCl (2.0 mmol), and base (2.0 mmol) were placed in flame-dried pyrex test tube and 10 ml of deoxygenated Me_2SO was added with stirring under nitrogen. The solution was irradiated with a 275-W sunlamp ca. 25 cm from the reaction tube for the period of time in the Table I. The reaction mixture was then poured into 15 ml of saturated sodium thiosulfate solution and extracted three times with methylene chloride or ether (10 ml each). The combined organic extract was washed three times with 10% sodium thiosulfate, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The mixture was analyzed by GC and each compound was isolated by flash column chromatography (hexane : ethyl acetate = 99 : 1) and characterized by instrumental analysis.

7. Photostimulated reaction of o-hydroxycinnamic acid with *t*-BuHgCl/KOH

The mixture of *o*-hydroxycinnamic acid (0.5 mmol), *t*-BuHgCl (2.0 mmol), and KOH (4.0 mmol) in 10 ml of deoxygenated Me_2SO or DMF was irradiated under nitrogen for 6 hours. After irradiation, the solution was worked up as previously described for oxidative alkylations of coumarin and yields were determined by GC analysis with toluene (0.5 equiv) as an internal standard and isolated by flash column chromatography (hexane : ethyl acetate = 96 : 4). (*E*)-2-(3,3-dimethyl-1-butenyl)phenol yielded 50% in Me_2SO and 60% in DMF.

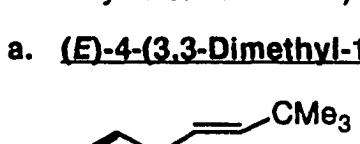
a. (*E*)-2-(3,3-Dimethyl-1-butenyl)phenol (6) Compound **6** was isolated as an oily liquid; ^1H NMR ($CDCl_3$) δ 1.14 (s, 9H), 4.93 (s, 1H), 6.21 (d, 1H, J = 16.2 Hz), 6.49 (d, 1H, J = 16.2 Hz), 6.78 (d, 1H, J = 7.8 Hz), 6.88 (t, 1H, J = 7.8 Hz), 7.08 (broad t, 1H), 7.31 (broad d, 1H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ

152.5 , 144.5, 128.0, 127.3, 125.2, 120.9, 118.9, 115.7, 33.8, 29.7 ppm; GCMS m/z (relative intensity) 176(M^+, 55), 161 (88), 133 (100), 107 (72), 91 (30), 77 (20); HRMS m/z cald for $C_{12}H_{16}O$ 176.1201, found 176.1200.

8. Photostimulated reaction of *p*-hydroxycinnamic acid with *t*-BuHgCl/KOH

Repitition of the previous experiment with a 9 hour irradiation period and work up as above produced 60% of (*E*)-4-(2,2-dimethyl-1-propenyl)-phenol in Me_2SO and 71% in DMF which were determined by GC analysis with toluene (0.5 equiv) as an internal standard and isolated by flash column chromatography (hexane : ethyl acetate = 96 : 4).

a. (*E*)-4-(3,3-Dimethyl-1-butenyl)phenol



Isolated material was a white solid, mp 101 - 103 °C; ^1H NMR ($CDCl_3$) δ 1.11 (s, 9H), 4.70 (s, 1H), 6.11 (d, 1H, J = 16.2 Hz), 6.24 (d, 1H, J = 16.2 Hz), 6.81 (broad d, 2H, J = 8.7 Hz), 7.25 (broad d, 2H, J = 8.7 Hz); GCMS m/z (relative intensity) 176 (M^+, 39), 161 (100), 146 (10), 133 (11), 115 (5), 107 (19), 91 (7), 77 (7), 57 (2); HRMS m/z cald for $C_{12}H_{16}O$ 176.1201, found 176.1199.

9. Photostimulated reaction of coumarin with *i*-PrHgCl in the presence of Dabco

The mixture of coumarin (0.5 mmol), *i*-PrHgCl (2.0 mmol), and Dabco (2.0 mmol) in 10 ml of Me_2SO was irradiated under nitrogen. After irradiation, the solution was worked up and analyzed by GC and isolated as previously

described for oxidative alkylations of coumarin to give 70% of 3-isopropylcoumarin (**7**) and 15% of 4-isopropylcoumarin (**8**).

a. <u>3-Isopropylcoumarin (7)</u>[55] Compound 7 was isolated as a white solid, mp 50 - 53 °C; ^{1}H NMR ($CDCl_3$) δ 1.27 (d, 6H, *J* = 6.9 Hz), 3.12 (d of sept., 1H, *J* = 0.6, 6.9 Hz), 7.22 - 7.32 (m, 2H), 7.42 - 7.48 (m, 3H); GCMS m/z (relative intensity) 188 (M^+, 65), 173 (100), 160 (40), 145 (26), 128 (13), 115 (28), 91 (10); HRMS m/z cald for $C_{12}H_{12}O_2$ 188.0837, found 188.0844; FTIR ($CDCl_3$) 2968 (m), 1722(s), 1709 (vs) cm^{-1} .

b. <u>4-Isopropylcoumarin (8)</u>[56] Compound 8 was identified by ^{1}H NMR and GCMS and confirmed by comparison of spectral data in literature;[56] ^{1}H NMR ($CDCl_3$) δ 1.34 (d, 6H, *J* = 6.9 Hz), 3.32 (sept., 1H, *J* = 6.9 Hz), 6.33 (s, 1H), 7.26 - 7.37 (m, 1H), 7.49 - 7.55 (m, 1H), 7.67 - 7.71 (dd, 1H, *J* = 1.2, 8.1 Hz); GCMS m/z (relative intensity) 188 (M^+, 54), 173 (4), 159 (6), 145 (100), 115 (16), 91 (8).

10. <u>General Procedure for photostimulated alkylations of *N*-methylmaleimide</u>

N-Methylmaleimide (0.5 mmol), RHgX (2.0 mmol), and coreactants (2.0 - 4.0 mmol of KI, 1.0 mmol of $K_2S_2O_8$ and/or 4 - 8 mmol of Dabco) were dissolved in 10 ml of deoxygenated Me_2SO in a pyrex tube equipped with a rubber septum. The mixture is irradiated under nitrogen by a 275-W GE sunlamp ca. 25 cm from the reaction tube for the period time shown in the Tables II and III. The reaction was quenched with aqueous sodium thiosulfate and extracted with ether. The ether extract was washed with aqueous sodium thiosulfate, dried over $MgSO_4$ and the solvent evaporated. The GC yield was determined with an internal

standard (toluene, 0.5 equiv) with the products isolated by flash chromatography (silica gel) with ethyl acetate (10%) - hexane (90%).

a. 3-(1,1-Dimethylethyl)-1-methyl-2,5-pyrrolydinedione (9)

Compound 9 was isolated as a white solid, mp 46 - 48 °C; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9H), 2.52 (dd, 1H, *J* = 16.8, 3.6 Hz), 2.63 (dd, 1H, *J* = 8.7, 3.6 Hz), 2.71 (dd, 1H, *J* = 16.8, 8.7 Hz), 2.96 (s, 3H); GCMS m/z (relative intensity) 169 (M^+, 1), 113 (100), 85 (23), 69 (31), 57 (26), 41 (51); HRMS m/z cald for $C_9H_{15}NO_2$ 169.1103, found 169.1100; FTIR ($CDCl_3$) 1774 (w),1697 (s) 1435 (m), 1291 (m) cm^{-1}.

b. 3-(1,1-Dimethylethyl)-1-methyl-1*H*-pyrrole-2,5-dione (10)

Compound 10 was isolated as a white solid, mp 53 - 55°C; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9H), 2.97 (s, 3H), 6.21 (s,1H); GCMS m/z (relative intensity) 167 (M^+, 56), 152 (40), 110 (30), 95 (70), 67 (100),; HRMS m/z cald for $C_9H_{13}NO_2$ 167.0946, found 167.0948; FTIR ($CDCl_3$) 1765 (w), 1707 (s), 1447 (m), 1389 (m) cm^{-1}.

c. 1-Methyl-3-(1-methylethyl)-2,5-pyrrolidinedione (11) Compound 11 was isolated as a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.87 (d, 3H, *J* = 6.6 Hz), 1.00 (d, 3H, *J* = 6.6 Hz), 2.25 - 2.38 (m, 1H), 2.45 (dd, 1H, *J* = 4.5, 18.0 Hz), 2.68 (dd, 1H, *J* = 9.0, 18.0 Hz), 2.79 (dd, 1H, *J* = 4.5, 9.0 Hz), 2.98 (s, 3H); GCMS m/z (relative intensity) 155 (M^+, 4), 140 (6), 113 (100), 85 (19), 55 (48);HRMS m/z cald for $C_8H_{13}NO_2$ 155.0946, found 155.0942; FTIR (neat) 2962 (w), 1760 (w), 1685 (s) cm^{-1}.

d. 1-Methyl-3-(methylethyl)-1-1*H*-pyrrole-2,5-dione (12)

Compound 12 was only identified by GC and GCMS because of separation problem. GCMS m/z (relative intensity) 153 (M^+, 100), 138 (31), 96 (47), 81 (76), 67 (65).

e. 1-Methyl-3-(1-methylethylidene)-2,5-pyrrolidinedione (13)

Compound 13 was isolated as a white solid, mp 104 -105 °C; ^{1}H NMR ($CDCl_3$) δ 1.88 (d, 3H), 2.35 (s, 3H), 3.02 (s, 3H), 3.20 (s, 2H); GCMS m/z (relative intensity) 153 (M^+, 71), 96 (23), 68 (100), 67 (52); HRMS m/z cald for $C_8H_{11}NO_2$ 153.0790, found 153.0793; FTIR ($CDCl_3$) 2914 (w), 1761 (m), 1701 (s), 1670 (m), 1437 (m), 1385 (m) cm^{-1}.

f. 3,4-Bis(1-methylethyl)-1-methyl-1*H*-pyrrole-2,5-dione (14)

Compound 14 was isolated as a white solid, mp 42 - 44 °C; ^{1}H NMR ($CDCl_3$) δ 1.28 (d, 12H, J = 6.9 Hz), 2.93 (s, 3H), 3.00 (hept., 2H, J = 6.9 Hz); GCMS m/z (relative intensity) 195 (M^+, 70), 180 (47), 166 (100), 138 (24), 95 (74), 41 (45); HRMS m/z cald for $C_{11}H_{17}NO_2$ 195.1529, found 195.1529; FTIR ($CDCl_3$) 1763 (w), 1699 (s) cm^{-1}.

11. Procedure for in situ reductive alkylation of the oxidative alkylation product (10)

The mixture of *N*-methylmaleimide (0.5 mmol), *t*-BuHgCl (2.0 mmol), and Dabco (2.0 mmol) in 10 ml of deoxygenated Me_2SO under nitrogen was irradiated for 4 hours in the usual manner. Then KI (2.0 mmol) was added to the reaction mixture and irradiation cintinued for 3 hours more. After the work up as previously described, the GC yield was determined and products were isolated. The reaction gave 13% of 9, 45% of 10, and 23% of mixture of *E*- and *Z*-3,4-bis-(1,1-dimethylethyl)-1-methyl-2,5-pyrrolidinedione(15).

a. (*E*)-3,4-Bis(1,1-dimethylethyl)-1-methyl-2,5-pyrrolidinedione (15a) Compound 15a was isolated as a white solid, mp 128 - 131 °C; ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 18H), 2.37 (s, 2H), 2.94 (s, 3H); GCMS m/z (relative intensity),

225 (M^+, 0.2), 210 (2), 169 (20), 113 (100), 57 (14); HRMS, m/z cald for $C_{13}H_{23}NO_2$ 225.1729, found 225.1730; FTIR ($CDCl_3$) 2963 (m), 1692 (s) cm^{-1}.

b. (Z)-3,4-Bis(1,1-dimethylethyl)-1-methyl-2,5-pyrrolidinedione (15b) Compound 15b was isolated as a white solid, mp 74 - 87 °C; ^1H NMR ($CDCl_3$) δ 1.20 (s, 18H), 2.80 (s, 2H), 2.93 (s, 3H); GCMS m/z (relative intensity), 225 (M^+, 0.1), 210 (1), 169 (18), 113 (100), 57 (25); CI (NH_3) 226 (MH^+); HRMS m/z cald for $C_{13}H_{23}NO_2$ 225.1729, found 225.1721, m/z cald for $C_{12}H_{20}NO_2$ (M - Me) 210.1494, found 210.1491; FTIR ($CDCl_3$) 2963 (m), 1769 (w), 1699 (s) cm^{-1}.

12. General procedure for photostimulated alkylations of 3-*tert*-butyl-*N*-methylmaleimde by RHgX

3-*tert*-Butyl-*N*-methylmaleimde (0.5mmol), RHgX and coreactants were dissolved in 10 ml of deoxygenated Me_2SO in a pyrex tube equipped with a rubber septum. The mixture was irradiated under nitrogen by a 275-W GE sun lamp ca. 25 cm from the reaction tube. The reaction was quenched with aqueous sodium thiosulfate and extracted with ether. The ether extract was washed three times with aqueous sodium thiosulfate, dried over $MgSO_4$, and the solvent evaporated. The GC yield was determined with an internal standard (toluene) and if necessary, the products were isolated by flash column chromatography (silica gel) with ethyl acetate (10%) - hexane (90%). The results are reported in Tables IV and V. (*E*)- and (*Z*)-3-*tert*-butyl-4-isopropyl-1-methyl-2,5-pyrrolidinedione (16a and b) and 3-*tert*-butyl-4-isopropyl-1-methyl-1*H*-pyrrole-2,5-dione (17) were analyzed as a crude mixture since they were failed to separate as pure compounds upon flash column chromatography.

a. (*E*)- and (*Z*)-3-*tert*-Butyl-4-isopropyl-1-methyl-2,5-pyrrolidinedione (16) (*E*)- and (*Z*)- isomers which were not separable were analyzed as a crude mixture by the ^{1}H NMR, GCMS, and GC retention time. For (*E*)-isomer, in ^{1}H NMR ($CDCl_3$), the *tert*-butyl group (9H) appeared at δ 1.00 and N-CH_3 at δ 2.95(3H); GCMS m/z (relative intensity) 211 (M^+, 1), 196 (2), 169 (4), 154 (47), 112 (100). For (*Z*)-isomer, in ^{1}H NMR ($CDCl_3$), the *tert*-butyl group (9H) appeared at δ 1.21 and N-CH_3 appeared at δ 2.94 (3H); GCMS m/z (relative intensity) 211 (M^+, 1), 196 (2), 169 (6), 112 (100).

b. 3-*tert*-Butyl-4-isopropyl-1-methyl-1*H*-pyrrole-2,5-dione (17) The ^{1}H NMR of 17 was assigned with impurities because of separation problem.; ^{1}H NMR ($CDCl_3$) δ 1.30 (d, 6H, J = 6.9 Hz), 1.38 (s, 9H), 2.92 (s, 3H), 3.43 (sept., 1H, J = 6.9 Hz); GCMS m/z (relative intensity) 209 (M^+, 43), 194 (30), 180 (11), 166 (100), 152 (40), 137 (25), 109 (61).

13. General procedure for photostimulated reductive and oxidative alkylations of 1,4-naphthoquinone

Reductive alkylations were carried out as previously described for photostimulated alkylations of *N*-methylmaleimde in 10 ml of Me_2SO or 12 ml of benzene with or without 4 - 5 vol% of H_2O or AcOH for the period of time in Tables VI, VII, VIII, and IX. The same work up procedure as described for photostimulated alkylations *N*-methylmaleimide was employed. In all cases, ether was used as an extraction solvent. In Me_2SO, only oxidative alkylation products were observed.

Oxidative alkylations were carried out as follows. 1,4-Naphthoquinone (0.5 mmol) and RHgCl (2.0 ~ 4.0 mmol) with or without co-reactants (2.0 mmol of

KI or NaI, and/or 1.0 mmol of $(NH_4)_2S_2O_8$ or $K_2S_2O_8$) were dissolved in 5 ml of Me_2SO or 6 ml of benzene which have been deoxygenated in a pyrex tube equipped with a rubber septum. The mixture was irradiated under nitrogen by a 275-W GE sunlamp ca. 25 cm from the reaction tube. Dabco (1.0 - 2.0 mmol) in 5 ml of Me_2SO or 6 ml of benzene was introduced dropwise over a 2 hour period by a syringe pump with irradiation . After the period of time mentioned in Tables VI, VII, and VIII, the reaction was quenched with aqueous sodium thiosulfate and extracted with ether (15 ml x 3). The ether extract was washed with aqueous sodium thiosulfate (40 ml x 3), dried over $MgSO_4$, and the solvent evaporated. The GC yield is determined with toluene internal standard and the products isolated by flash column chromatography (silica gel) with ethyl acetate (1 - 5%) - hexane (95 - 99%).

a. **2-*tert*-Butyl-2,3-dihydro-1,4-naphthoquinone (18)** Compound **18** was isolated as a dark brown liquid; ^1H NMR ($CDCl_3$) δ 0.99 (s,9H), 2.89 (t, 1H, J = 5.7 Hz), 3.13 (d, 2H, J = 5.7 Hz). 7.68 - 7.77 (m, 2H), 7.99 - 8.05 (m, 2H); ^1H NMR (Me_2SO-d_6) δ 0.92 (s, 9H), 2.95 (t or dd, 1H, J = 6.0 Hz), 3.05 (dd, 1H, J = 16.8, 5.7 Hz), 3.27 (dd, 1H, J = 16.8, 6.3 Hz), 7.80 - 7.89 (m, 2H), 7.89 - 7.95 (m, 2H); GCMS m/z (relative intensity) 216 (M^+,0.02), 214 (0.3), 201 (2), 183 (2), 160 (100), 132 (12), 104 (8), 57 (26); CI (NH_3) 217 (MH^+); HRMS m/z cald for $C_{14}H_{17}O_2$ (M + H) 217.1229, found 217.1230, m/z cald for $C_{13}H_{13}O_2$ (M - Me) 201.0916, found 201.0912; FTIR (neat) 3072 (w), 2968 (m), 2910 (w), 1695 (vs), 1595 (m), 1292 (m) cm^{-1}.

b. **2-*tert*-Butyl-1,4-naphthoquinone (19)**[57,58] Compound **19** was isolated as a oily dark brown liquid; ^1H NMR ($CDCl_3$) δ 1.38 (s, 9H), 6.85 (s, 1H), 7.74 - 7.65 (m, 2H), 8.00 - 8.10 (m, 2H) ; GCMS m/z (relative intensity) 214

(M^+,100), 199 (48), 171 (35), 159 (25), 144 (16), 128 (37), 105 (42), 76 (36), 57 (7); HRMS m/z cald for $C_{14}H_{14}O_2$ 214.0994, found 214.0997 FTIR ($CDCl_3$) 3071 (w), 1686 (S), 1664 (vs), 1597 (m) cm^{-1}.

c. 2-Isopropyl-1,4-naphthoquinone (20)[57,59] Compound 20 was isolated as a oily yellow liquid; ^1H NMR ($CDCl_3$) δ 1.21 (d, 6H, J = 6.9 Hz), 3.25 (sept. of d, 1H, J = 6.9, 0.9 Hz), 6.77 (d, 1H, J = 0.9 Hz), 7.70 - 7.76 (m, 2H), 8.04 - 8.13 (m, 2H); GCMS m/z (relative intensity) 200 (M^+, 100), 185 (24), 172 (17), 157 (30), 129 (28), 105 (15), 76 (37) ; HRMS m/z cald for $C_{13}H_{12}O_2$ 200.0837, found 200.0838; FTIR ($CDCl_3$) 3076 (w), 2970 (w), 2934 (w), 1664 (s), 1595 (m) cm^{-1}.

d. 2,3-Dihydro-2-isopropyl-1,4-naphthoquinone (21) Compound 21 was isolated as an oily dark brown liquid; ^1H NMR ($CDCl_3$) δ 0.98 (dd, 6H, J = 6.6, 1.2 Hz), 2.28 (octet, 1H, J = 6.6 Hz), 2.83 - 2.90 (m, 1H), 2.95 - 3.13 (m, 2H), 7.68 - 7.75 (m, 2H), 7.95 - 8.07 (m, 2H); GCMS m/z (relative intensity) 202 (M^+, 5), 187 (16), 160 (100), 131 (23), 104 (30), 76 (31); HRMS m/z cald for $C_{13}H_{14}O_2$ 202.0994, found 202.0990; FTIR (neat) 3070 (w), 2966 (m), 2910 (w), 1693 (vs), 1595 (m) cm^{-1}.

e. 2,3-Diisopropyl-1,4-naphthoquinone (22) Compound 22 was identified by GC and GCMS only; GCMS (relative intensity) 242 (M^+, 100), 227 (35), 185 (20), 105 (19), 76 (29), 43 (49).

f. 2-Butyl-1,4-naphthoquinone (23)[60] Compound 23 was isolated as a dark yellow oily liquid; ^1H NMR ($CDCl_3$) δ 0.96 (t, 3H, J = 7.2 Hz), 1.42 (hex., 2H, J = 7.2 Hz), 1.57 (broad quint., 2H, J = 7.2 Hz), 2.57 (dt, 2H, J = 1.2, 7.2 Hz), 6.79 (t, 1H, J = 1.2 Hz), 7.69 - 7.76 (m, 2H), 8.02 - 8.04 (m, 2H); GCMS (relative intensity) 214 (M^+, 69), 199 (24), 172 (100), 144 (48), 115 (38), 76 (39); HRMS

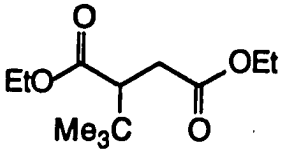
m/z cald for $C_{14}H_{14}O_2$ 214.0994, found 214.0997; FTIR ($CDCl_3$) 2961 (w) 2930 (w) 2868 (w) 1661 (vs), 1653 (s) cm^{-1}.

g. 2,3-Dibutyl-1,4-naphthoquinone (24) Compound 24 was isolated as a brown oily liquid; ^1H NMR ($CDCl_3$) δ 0.96 (t, 6H, J = 7.2 Hz), 1.40 - 1.55 (m, 8H), 2.61 (broad t, 4H, J = 7.2 Hz), 7.68 (dd, 2H, J = 5.7, 2.4 Hz), 8.07 (dd, 2H, J = 5.7, 2.4 Hz); GCMS m/z (relative intensity) 270 (M^+, 100), 229 (42), 213 (38), 186 (42), 159 (23),115 (17); HRMS m/z cald for $C_{18}H_{22}O_2$ 270.1620, found 270.1617; FTIR ($CDCl_3$) 3074 (w), 2961 (m), 2932 (m), 1695 (m), 1661 (vs), 1597 (m) cm^{-1}.

14. General procedure for photostimulated alkylations of 1,4-enediones and α,β-unsaturated carbonyl compounds by RHgX

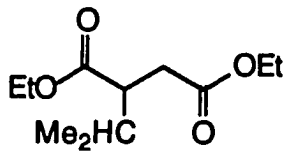
The substrate (0.5mmol), RHgX and coreactants were dissolved in 10 ml of deoxygenated Me_2SO in a pyrex tube equipped with a rubber septum. The mixture was irradiated under nitrogen by a 275-W GE sun lamp ca. 25 cm from the reaction tube. The reaction was quenched with aqueous sodium thiosulfate and extracted with ether. The ether extract was washed three times with aqueous sodium thiosulfate, dried over $MgSO_4$, and the solvent evaporated. The GC yield was determined with an internal standard (toluene) and if necessary, the products were isolated by flash column chromatography (silica gel) with ethyl acetate (1 - 2%) - hexane (98 - 99%).

a. Diethyl 2-(1,1-dimethylethyl)succinate[61]



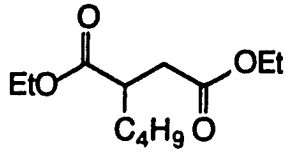
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9H), 1.24 (t, 3H, *J* = 7.2 Hz), 1.27 (t, 3H, *J* = 7.2 Hz), 2.46 (dd, 1H, *J* = 3.0, 16.2 Hz), 2.61 (dd, 1H, *J* = 3.0, 12.0 Hz), 2.78 (dd, 1H, *J* = 12.0, 16.2 Hz), 4.07 - 4.21 (m, 4H); GCMS m/z (relative intensity) 231 (M^+ + 1, 0.2), 215 (0.4), 185 (42), 174 (43), 128 (100), 111 (14), 100 (26), 83 (16), 69 (15), 57 (31); HRMS m/z cald for $C_{12}H_{22}O_4$ 230.1518, found 230.1515; FTIR ($CDCl_3$) 2968 (m), 2907 (w), 1728 (s), 1161 (s) cm^{-1}.

b. <u>Diethyl 2-(1-methylethyl)succinate</u>[61]



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.93 (d, 3H, *J* = 6.9 Hz), 0.95 (d, 3H, *J* = 6.9 Hz),1.24 (t, 3H, *J* = 6.9 Hz),1.26 (t, 3H, *J* = 6.9 Hz), 1.93 - 2.05 (m, 1H), 2.40 (dt, 1H, *J* = 12.9, 8.4 Hz), 2.65 - 2.77 (m, 2H), 4.08 - 4.22 (m, 4H); GCMS m/z (relative intensity) 216 (M^+, 0), 171 (100), 155 (10), 143 (33), 128 (90), 115 (21), 101 (62), 69 (85), 55 (70), 41 (56); CI(NH_3) = 217 (MH^+); HRMS m/z cald for $C_9H_{15}O_3$ (M - 45) 171.1021, found 171.1022, cald for $C_{10}H_{17}O_4$ (M - 15) 201.1127, found 201.1131; FTIR (neat) 2966 (m), 2937 (s), 1734 (s) 1177 (s) cm^{-1}.

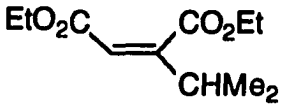
c. <u>Diethyl 2-butylsuccinate</u>[62]



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H, *J* = 6.9 Hz), 1.22 - 1.70 (m, 12H, which includes two triplet at 1.25 and 1.26, *J* = 7.2 Hz),

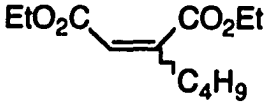
2.41 (dd, 1H, J = 5.1, 16.2 Hz), 2.70 (dd, 1H, J = 9.0, 16.2 Hz), 2.76 - 2.87 (m, 1H), 4.09 - 4.20 (m, 4H); GCMS m/z (relative intensity) 230 (M^+, 0.2), 185 (47), 174 (24), 157 (14), 143 (45), 128 (75), 111 (45), 83 (59), 55 (100); HRMS m/z cald for $C_{12}H_{22}O_4$ 230.1518, found 230.1515; FTIR (neat) 2961 (m), 2935 (m), 1736 (s), 1163 (s) cm^{-1}.

d. <u>(Z)-Diethyl 2-(1-methylethyl)butenedioate</u>[63]



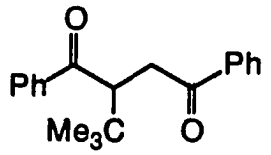
The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 1.21 (d, 6H, J = 6.9 Hz), 1.22 - 1.35 (m, 6H), 3.77 (sept., 1H, J = 6.9 Hz), 4.17 - 4.28 (m, 4H), 6.45 (s,1H); GCMS m/z (relative intensity) 214 (M^+, 0), 168 (46), 140 (72), 112 (100), 95 (18), 67 (36), 43 (52); CI(NH_3) = 215 (MH^+); HRMS m/z cald for $C_9H_{12}O_3$ (M - EtOH) 168.0786, found 168.0790; FTIR (neat) 2982 (m), 2939 (w), 1724 (vs), 1636 (m), 1250 (s) cm^{-1}.

e. <u>Diethyl 2-butyl-betutenedioate</u>[63]



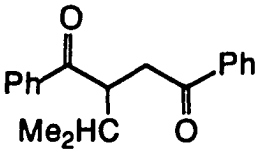
The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 0.92 (t, 3H, J = 7.2 Hz), 1.28 - 1.50 (m, 10H, which includes two triplet at 1.31 and 1.32 with J = 7.2 Hz), 2.97 (t, 2H, J = 7.5 Hz) 4.24 (quint. or dq, 4H, J = 7.2 Hz), 6.72 (s, 1H); GCMS m/z (relative intensity) 228 (M^+, 0.1), 182 (81), 154 (56), 140 (21), 126 (54), 112 (100), 97 (28), 81 (79); HRMS m/z cald for $C_{12}H_{20}O_4$ 228.1362, found 228.1358; FTIR ($CDCl_3$) 2957 (m), 2926 (m), 1716 (s) cm^{-1}.

f. 2-(1,1-Dimethylethyl)-1,4-diphenyl-1,4-butanedione



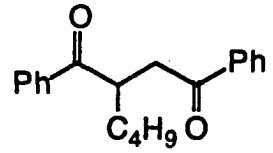
The compound was isolated as a pale yellow solid, mp 78 - 80 °C; ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 9H), 3.23 (dd, 1H, J = 2.4, 17.7 Hz), 3.88 (dd, 1H, J = 11.1, 17.7 Hz), 4.52 (dd, 1H, J = 2.4, 11.1 Hz), 7.40 - 7.57 (m, 6H), 7.97 - 7.94 (m, 2H), 8.10 - 8.14 (m, 2H); GCMS m/z (relative intensity) 294 (M^+, 1), 279 (0.1), 238 (4), 224 (2), 189 (1), 175 (2), 133 (8), 105 (100), 77 (25), 57 (3) HRMS m/z cald for $C_{20}H_{22}O_2$ 294.1620, found 294.1617; FTIR ($CDCl_3$) 3063 (w), 2963 (m), 1675 (s) cm^{-1}.

g. 1,4-Diphenyl-2-(1-methylethyl)-1,4-butanedione



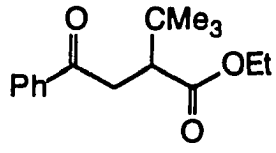
The compound was isolated as an oily liquid; ^{1}H NMR ($CDCl_3$) δ 0.98 (d, 3H, J = 6.9 Hz), 1.02 (d, 3H, J = 6.9 Hz), 2.06 - 2.20 (m, 1H, including J = 5.1, 6.9 Hz), 3.11 (dd, 1H, J = 3.0, 18.0 Hz), 3.79 (dd, 1H, J = 10.2, 18.0 Hz), 4.06 (ddd, 1H, J = 3.0, 5.1, 10.2 Hz), 7.40 - 7.59 (m, 6H), 7.96 - 8.08 (m, 4H); GCMS m/z (relative intensity) 280 (M^+, 2), 238 (1), 161 (23), 105 (100), 77 (37); HRMS m/z cald for $C_{19}H_{20}O_2$ 280.1463, found 280.1460; FTIR (neat) 3061 (w), 2963 (m), 2932 (w), 1680 (vs), 1597 (m), 1582 (w) cm^{-1}.

h. **2-Butyl-1,4-diphenyl-1,4-butanedione**



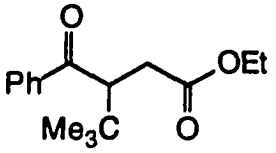
The compound was isolated as a oily liquid; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 6.9 Hz), 1.25 - 1.38 (m, 4H), 1.49 - 1.60 (m, 1H), 1.71 - 1.81 (m, 1H), 3.16 (dd, 1H, J = 4.2, 18.0 Hz), 3.72 (dd, 1H, J = 9.0, 18.0 Hz), 4.07 - 4.18 (m, 1H); GCMS m/z (relative intensity) 294 (M^+, 1), 238 (11), 175 (13), 105 (100), 77 (35); HRMS m/z cald for $C_{20}H_{22}O_2$ 294.1984 found 294.1976; FTIR ($CDCl_3$) 3062 (w), 2957 (m), 2927 (m), 2858 (w), 1679 cm^{-1} (s).

i. **Ethyl 2-(1,1-dimethylethyl)-4-oxo-benzenebutanoate**



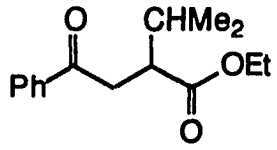
The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9H), 1.27 (t, 3H, J = 7.2 Hz), 2.83 (dd, 1H, J = 2.7, 11.4 Hz), 3.08 (dd, 1H, J = 2.7, 17.7 Hz), 3.53 (dd, 1H, J = 11.4, 17.7 Hz), 4.15 (dd,2H, J = 0.9, 7.2 Hz), 7.42 - 7.58 (m, 3H), 7.94 - 7.98 (m, 2H); GCMS m/z (relative intensity) 262 (M^+, 0.1), 217 (9), 206 (14), 161 (14), 105 (100), 77 (45); HRMS m/z cald for $C_{16}H_{22}O_3$ 262.1569, found 262.1570; FTIR (neat) 2963 (m), 2872 (w), 1726 (s), 1690 (s) cm^{-1}.

j. **Ethyl 3-(1,1-dimethylethyl)-4-oxo-benzenebutanoate**



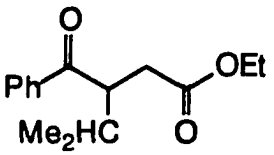
The compound was identified by ^1H NMR, and GCMS only; ^1H NMR ($CDCl_3$) δ 0.92 (s,9H of *tert*-butyl group); GCMS m/z (relative intensity) 262 (M^+, 0.1), 206 (13), 160 (5), 133(7), 105 (100), 77 (23)

k. **Ethyl 2-(1-methylethyl)-4-oxo-benzenebutanoate**



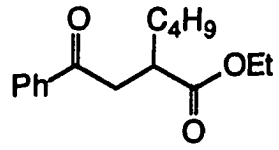
The compound was isolated as a liquid (85% pure with 15% of regioisomer); ^1H NMR ($CDCl_3$) δ 1.00 (d, 6H, *J* = 6.9 Hz), 1.25 (t, 3H, *J* = 6.9 Hz), 2.08 (sept. 1H, *J* = 6.6 Hz), 2.90 - 3.03 (m, 2H), 3.50 (dd, 1H, *J* = 11.1, 18.3 Hz), 4.15 (dq, 2H, *J* = 3.0, 7.2 Hz), 7.42 - 7.58 (m, 3H), 7.95 - 8.00 (m, 2H); GCMS m/z (relative intensity) 248 (M^+, 0.2), 203 (9), 129 (29), 105 (100), 77 (37); HRMS m/z cald for $C_{15}H_{20}O_3$ 248.1413, found 248.1411; FTIR (neat) 3065 (w), 2964 (m), 2934(w), 1730 (vs), 1688 (s) cm^{-1}.

l. **Ethyl 3-(1-methylethyl)-4-oxo-benzenebutanoate**



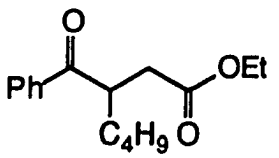
The compound was identified by crude ^1H NMR and GCMS as a major reaction product after separation; ^1H NMR ($CDCl_3$) δ 0.94 (d, 6H, *J* = 6.9 Hz), 1.16 (t, 3H, *J* = 6.9 Hz),2.0 - 2.15 (m, 1H overlapped with regioisomer), 2.49 (dd, 1H, *J* = 3.6, 16.8 Hz), 3.44 - 3.54 (m, 1H overlapped with regioisomer), 3.78 - 3.85 (m, 1H), 4.05 (q, 2H, *J* = 7.2 Hz), 7.40 - 7.60 (m, 3H), 7.90 - 8.00 (m, 2H); GCMS m/z (relative intensity) 248 (M^+, 0.9), 203 (7), 160 (7), 133(3), 105 (100), 77 (24).

m. **Ethyl 2-butyl-4-oxo-benzenebutanoate**



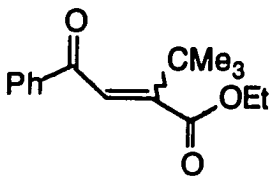
The compound was identified by ^{1}H NMR and GCMS as a major product (80%) after separation because a regioisomer was not separable; ^{1}H NMR ($CDCl_3$) δ 3.0 - 3.1 (m, including dd, J = 18.6, 4.5 Hz, one of PhC$\underline{H_2}$), 3.46 (dd, 1H, J = 18.6, 10.2 Hz, one of PhC$\underline{H_2}$); GCMS m/z (relative intensity) 262 (M^+, 2), 217 (7), 188 (3), 143 (19), 120 (42), 105 (100), 77 (41).

n. **Ethyl 3-butyl-4-oxo-benzenebutanoate**



The compound was identified by ^{1}H NMR and GCMS as a minor product (20%) after separation because a regioisomer was not separable; ^{1}H NMR ($CDCl_3$) δ 2.51 (dd, 1H, J = 16.8, 4.8 Hz, one of $EtO_2CC\underline{H_2}$), 2.94 (dd, 1H, J = 16.8, 9.6 Hz, one of $EtO_2CC\underline{H_2}$); GCMS m/z (relative intensity) 262 (M^+, 0.3), 217 (5), 206 (16), 160 (4), 105 (100), 77 (27).

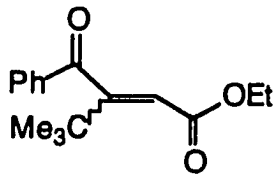
o. **Ethyl 2-(1,1-dimethylethyl)-4-oxo-4-phenylbutenoate**



The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 9H), 1.29 (t, 3H, J = 7.2 Hz) 4.29 (q, 2H, J = 7.2 Hz), 6.88 (s, 1H), 7.43 - 7.59 (m, 3H), 7.90 -

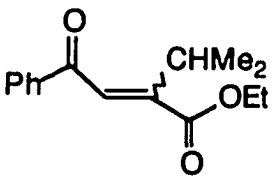
7.94 (m, 2H); GCMS m/z (relative intensity) 260 (M^+,2), 215 (19), 187 (57), 145 (23), 105 (100), 77 (55), 57 (13) HRMS m/z cald for $C_{16}H_{20}O_3$ 260.1413, found 260.1412; FTIR (neat) 2968 (m), 2908 (w), 1728 (vs), 1670 (s), 1609 (m) cm^{-1}.

p. Ethyl 3-(1,1-dimethylethyl)-4-oxo-4-phenylbutenoate



The compound was identified by ^1H NMR and GCMS as a major (67% pure after isolation); ^1H NMR($CDCl_3$) δ 1.21 (s, 9H), 1.35 (t, 3H, J = 6.9 Hz), 4.27 (q, 2H, J = 6.9 Hz), 6.83 (s, 1H), 7.44 - 7.63 (m, 3H), 7.94 - 8.04 (m, 2H); GCMS m/z (relative intensity) 260 (M^+, 3), 215 (118), 187 (53), 145 (21), 105 (100), 77 (62).

q. Ethyl 2-(1-methylethyl)-4-oxo-4-phenylbutenoate



The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 1.20 (d, 6H, J = 6.9 Hz), 1.39 (t, 3H, J = 6.9 Hz), 3.21 (sept., 1H, J = 6.9 Hz), 4.29 (q, 2H, J = 6.9 Hz), 7.38 (s, 1H), 7.46 - 7.63 (m, 3H), 7.94 - 7.98 (m, 2H); GCMS m/z (relative intensity) 246 (M^+, 1), 200 (14), 105 (100), 77 (31); HRMS m/z cald for $C_{15}H_{18}O_3$ 246.1256, found 246.1259; FTIR (neat) 3065 (w), 2968 (m), 2935 (w), 1718 (vs), 1688 (s), 1957 cm^{-1} (m).

r. Dihydro-(1,1-dimethylethyl)-2,5-furandione (25)[64] The compound **25** seemed to polymerize during flash column chromatographic separation. Thus it was identified by ^1H NMR and GCMS after the work up

without separation (purity >90%); ^{1}H NMR($CDCl_3$), δ 1.08 (s, 9H), 2.79 (dd, 1H, *J* = 3.3, 15.9 Hz), 2.85 - 3.02 (m, 2H); GCMS m/z (relative intensity) 157 (M^+ + 1, 0.02), 141 (M - CH_3), 100 (M - C_4H_8, 37), 84 (17), 69 (68), 57 (94), 41 (100).

s. (1,1-Dimethylethyl)-2,5-furandione (26)[65] The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$), δ 1.34 (s, 9H), 6.53 (s, 1H), GCMS m/z (relative intensity) 155 (M^+ + 1, 0.5), 154 (M^+, 0.1), 139 (7), 126 (65), 111 (41), 95 (42), 83 (50), 67 (90), 41 (100); HRMS m/z cald for $C_8H_{10}O_3$ 154.0630, found 154.0630; FTIR ($CDCl_3$) 2974 (w), 1850 (m), 1771 (s) cm^{-1}.

N-Methyl-2(1*H*)-quinolinone, the compound was prepared from 2-hydroxyquinoline and CH_3I/NaOH/MeOH/H_2O by known method.[66] It was isolated by flash column chromathography with ethyl acetate (40%) - hexane (60%). It was used for the photostimulated alkylations to produce 3-(1,1-dimethylethyl)-1-methyl-2(1*H*)-quinoline (**27**) and 1-methyl-3-(1-methylethyl)-2(1*H*)-quinoline (**28**) and each product was isolated by flash column chromatography (ethyl acetate : hexane = 20 : 80).

t. 3-(1,1-Dimethylethyl)-1-methyl-2(1*H*)-quinolinone (27) The compound **27** was isolated as an oily liquid by flash column chromathography (ethyl acetate : hexane = 30 : 70) followed by preparative TLC (ethyl acetate : methylene chloride = 3 : 97); ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 9H), 3.72 (s, 3H), 7.15 - 7.32 (m, 2H), 7.45 - 7.55 (m, 2H), 7.58 (s, 1H); GCMS m/z (relative intensity) 215 (M^+, 43), 200 (71), 173 (100), 159 (8), 144 (13), 130 (9), 115 (9), 100 (9), 93 (12); HRMS m/z cald for $C_{14}H_{17}NO$ 215.1310, found 215.1308; FTIR ($CDCl_3$) 2963 (m), 1639 (vs) cm^{-1}.

u. **1-Methyl-3-(1-methylethyl)-2(1*H*)-quinolininone (28)** The compound **28** was isolated as a liquid by flash column chromathography (ethyl acetate : hexane = 30 : 70); ^{1}H NMR ($CDCl_3$) δ 1.26 (d, J = 6.9 Hz, 6H) 3.31 (sept., 1H, J = 6.9 Hz) 3.75 (s, 3H), 7.18 - 7.34 (m, 2H), 7.45 - 7.55 (m, 3H, including singlet, 1H at 7.50); GCMS m/z (relative intensity) 201 (M^+, 53), 186 (100), 173 (64), 159 (6), 143 (10), 115 (11), 93 (11); HRMS m/z cald for $C_{13}H_{15}NO$ 201.1154, found 201.1148 FTIR ($CDCl_3$) 3050 (w), 2959 (m), 2869 (w), 1646 (vs), 1573 (s) cm^{-1}.

v. **2-(1,1-Dimethylethyl)-(1*H*)-phenalen-1-one (29)** Compound **29** was obtained by using perinaphthenone (0.5 mmol), *t*-BuOK (4.0 equiv), and *t*-BuHgCl (4 equiv) in 12 ml of benzene with the same reaction condition as described previously. A 40% yield was obtained in 20 h. The compound was isolated by flash column chromatography (ethyl acetate : hexane = 1 : 99) followed by preparative TLC (ethyl acetate : hexane = 5 : 95). The yellow needles had mp 89 - 90 °C; ^{1}H NMR ($CDCl_3$), δ 1.45 (s, 9H), 7.56 (dd, 1H, J = 0.9, 8.1 Hz), 7.63 (s, 1H), 7.68 - 7.78 (m, 2H), 7.94 (dd, 1H, J = 0.9, 8.1 Hz), 8.14 (dd, 1H, J = 0.9, 8.1 Hz), 8.60 (dd, 1H, J = 0.9, 7.5 Hz); GCMS m/z (relative intensity) 236 (M^+, 100), 221 (86), 207 (19), 194 (67), 181 (25), 165 (38), 152 (23), 89 (28), 57 (1); HRMS m/z cald for $C_{17}H_{16}O$ 236.1201 found 236.1201; FTIR ($CDCl_3$), 2961 (m), 1636 (vs), 1624 (s) cm^{-1}.

Phenyl vinyl ketone was prepared by the Grignard reaction with benzaldehyde and vinylmagnesium bromide in THF solution[67] followed by Jones oxidation.[68] Phenyl vinyl ketone was purified by distillation and used for the following reactions; ^{1}H NMR ($CDCl_3$) δ 5.93 (dd, 1H, J = 1.5, 10.2 Hz), 6.44

(dd, 1H, J = 1.5, 17.1 Hz), 7.16 (dd, 1H, J = 10.2, 17.1 Hz), 7.40 - 7.65 (m, 3H), 7.90 - 8.00 (m, 2H).

w. 4,4-Dimethyl-1-phenyl-1-pentanone (30)[69] The compound **30** was identified by ^{1}H NMR and GCMS after isolation and confirmed by comparison of spectral data with the literature;[70] ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 9H), 1.64 (m, 2H), 2.94 (m, 2H), 7.41 - 7.65 (m, 3H), 7.88 - 8.00 (m, 2H), GCMS m/z (relative intensity) 190 (M^+, 6), 175 (5), 133 (21), 105 (100), 77 (31), 57 (7).

x. Ethyl 4,4-Dimethyl-pentanoate (31)[71] The compound was identified by ^{1}H NMR and GCMS after isolaton and confirmed by comparison with the literature;[71] ^{1}H NMR ($CDCl_3$) δ 0.89 (s, 9H), 1.25 (t, 3H, J = 7.2 Hz), 1.51 - 1.59 (m, 2H), 2.23 - 2.30 (m, 2H), 4.11 (q, 2H, J = 7.2 Hz) GCMS m/z (relative intensity) 158 (M^+, 0.1), 143 (12), 114 (29), 101 (100), 71 (80), 57 (88), 41 (90).

y. Diethyl (1,2,2-trimethylpropyl)malonate (32) The compound **32** was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 9H), 1.01 (d, 3H, J = 7.2 Hz), 1.23 - 1.30 (m, 6H), 2.24 (dq, 1H, J = 5.4, 7.2 Hz), 3.51 (d, 1H, J = 5.4 Hz), 4.13 - 4.23 (m, 4H); GCMS m/z (relative intensity) 245 (M^+ + 1, 9), 229 (M - Me, 15), 199 (50), 142 (91), 115 (100), 57 (52); CI (NH_3) 245 (MH^+); HRMS m/z cald for $C_{13}H_{25}O_4$ (M + H) 245.1753, found 245.1753, m/z cald for $C_{12}H_{21}O_4$ (M - Me) 229.1434, found 229.1439; FTIR (neat) 2972 (m), 1755(s), 1732 (vs) cm^{-1}.

z. Diethyl (2,2-dimethyl-1-phenylpropyl)malonate (33) The compound **33** was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3H, J = 11.1 Hz), 0.88 (s, 9H), 1.30 (t, 3H, J = 6.9 Hz), 3.47 (d, 1H, J = 11.1 Hz), 3.71 (dq, 2H, J = 3.3, 6.9 Hz), 3.98 (d, 1H, J = 11.1 Hz), 4.22 (m, 2H, including J = 3.3, 6.9 Hz), 7.12 - 7.26 (m, 5H); GCMS (relative intensity) 307 (M^+ + 1, 0.12), 306 (M^+, 0.03), 291 (1), 250 (47), 176 (100), 131 (95), 91 (37), 57 (61); HRMS m/z cald for

$C_{18}H_{26}O_4$ 306.1831, found 306.1830; FTIR (neat) 2974 (m), 1759 (s), 1732 (vs) cm^{-1}.

N-Acryloylaniline, the aniline was prepared by known method by using aniline, acryloyl chloride and pyridine in ether[72] and used for the following reactions.

aa. **4,4-Dimethyl-*N*-phenylpentanamide (34)**[73] The compound **34** was isolated as a white solid, mp 138 - 139 °C; ^1H NMR ($CDCl_3$) δ 0.91 (s, 9H), 1.60 - 1.67 (m, 2H), 2.27 - 2.35 (m, 2H), 7.07 (t, 1H, J = 7.8 Hz), 7.28 (t, 2H, J = 7.8 Hz), 7.51 (d, 2H, J = 7.8 Hz), 7.58 (broad s, 1H); ^1H NMR (Me_2SO-d_6) δ 0.90 (s, 9H), 1.47 - 1.54 (m, 2H), 2.23 - 2.30 (m, 2H), 7.00 (t, 1H, J = 8.1 Hz), 7.27 (t, 2H, J = 8.1 Hz), 7.57 (d, 2H, J = 8.1 Hz), 9.86 (broad s, 1H); GCMS m/z (relative intensity) 205 (M^+, 6), 190 (4), 93 (100), 77 (5), 57 (10); HRMS m/z cald for $C_{13}H_{19}NO$ 205.1467, found 205.1461; FTIR ($CDCl_3$) 3435 (m), 2957 (m), 1682 (s) cm^{-1}.

ab. **2-Benzyl-3,3-dimethyl-1-phenyl-1-butanone (35)** The compound was isolated as a white solid, mp 109 - 112 °C; ^1H NMR ($CDCl_3$) δ 0.94 (s, 9H), 3.25 (dd, 1H, J = 3.9, 9.9 Hz), 3.34 (dd, 1H, J = 3.9, 16.5 Hz), 3.52 (dd, 1H, J = 9.9, 16.5 Hz), 7.84 - 7.87 (m, 2H), 7.38 - 7.54 (m, 3H), 7.12 - 7.26 (m, 5H); GCMS m/z (relative intensity) 266 (M^+, 0.2), 109 (100), 105 (80), 91 (24), 77 (29), 57 (8); ^{13}C ($CDCl_3$) for aliphatic carbons δ 28.21 (q), 33.80 (s), 39.80 (t), 51.05 (d), 199.46 (s) ppm; HRMS m/z cald for $C_{19}H_{22}O$ 266.1671, found 266.1667; IR ($CDCl_3$) 3027 (w), 2953 (m), 2921(m), 2860 (w), 1679 (s) cm^{-1}.

14. General procedure for deutration experiments

The substrate (chalcone or *N*-methylmaleimide), *t*-BuHgCl, and coreactants (KI with/without Dabco) in Me_2SO was irradiated as previously described for photostimulated reactions of enediones and α,β-unsaturated carbonyl compounds. After irradiation the reaction mixture was quenched with sodium thiosulfate/D_2O solution and extracted with ether. The extract was washed with aqueous sodium thiosulfate, dried over $MgSO_4$, and the solvent evaporated. The product was analyzed by ^1H NMR and GCMS after work up.

II. KINETIC CHAIN LENGTH AND RELATIVE REACTIVITIES OF ENONES TOWARDS *TERT*-BUTYL RADICAL

A. Kinetic Chain Length

Chemical kinetics and its supporting techniques have proved to be valuable approaches to the study of reaction mechanisms and to an understanding of chemical reactivity. A chain reaction is one whose mechanism involves low concentrations of reactive intermediates (chain carriers) which 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 propagating steps which can be interrupted by a termination step.

Kinetic chain length represents the average number of reactant molecules consumed for every radical which initiates a chain reaction.[74] Ultimately the initiation reaction must produce stable products via a number of chain propagation steps.[75] Therefore, the magnitude of a kinetic chain length can be a criterion to determine whether the reaction is a chain reaction or not. To calculate the kinetic chain length, the rate of chain initiation must be known. This rate is conveniently measured from the inhibition period observed with known amounts of free radical chain inhibitors. Free radical chain reactions are commonly susceptible to inhibition in which a mere trace of an inhibitor can cause a marked decrease in the initial reaction rate.

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 reaction of some radical R• with two substances A_1 and A_2 to give products P_1 and P_2.[75,76] If the rate constant is known for one of the substrates, the absolute rate constants can be calculated from relative reactivity data. In the direct competitive approach, one needs to design an experimental system in which R• can be generated in a mixture of A_1 and A_2. Suppose one added R• to a mixture of substances A_1 and A_2, both of which react with R•.

$$A_1 + R\bullet \xrightarrow{k_1} P_1 \qquad (34)$$

$$A_2 + R\bullet \xrightarrow{k_2} P_2 \qquad (35)$$

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

$d[P_2]/dt = k_2[A_2][R\bullet]$

Division gives $d[P_1]/d[P_2] = (k_1/k_2)([A_1]/[A_2])$ (36)

Equation 36 may consider in following two cases;

a) The case when $[A_1]$ and $[A_2]$ >> [P] and are then effectively constant, in which case the product ratio gives the constant ratio.

$$k_1/k_2 = [P_1]_\infty [A_2]_o/[P_2]_\infty [A_1]_o$$
$$= [P_1]_\infty /[P_2]_\infty \quad (\text{if } [A_1]_o = [A_2]_o) \qquad (37)$$

b) The case in which concentrations are not set such that $[A_1]$ and $[A_2]$ remain essentially 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

$$k_1/k_2 = \ln\{[A_1]_o/([A_1]_o - [P_1]_f)\}/\ln\{[A_2]_o/([A_2]_o - [P_2]_f)\} \qquad (38)$$

Use of eq. 37 or 38 permits determination of the relative rate ratios.

In this chapter, I will present the results on the determination of the kinetic chain length for the reaction of *N*-methylmaleimide with *t*-BuHgI and t-BuHgCl/KI in Me_2SO and a study of relative reactivities of various substrates including the effect of *p*-toluenesulfonic acid (PTSA) and trimethylsilyl iodide (TMSI) on the reactivity of imines and nitriles.

C. Results and Discussion

1. Determination of kinetic chain length of the reaction between *N*-methylmaleimide and *t*-BuHgX

The kinetic chain length (k.c.l.) of a reaction can be formulated as shown in eq. 39.

$$\text{k.c.l.} = \frac{\text{Initial reaction rate}}{\text{Rate of initiation}} \qquad (39)$$

The initial rate can be measured experimentally by following either the rate of consumption of the substrate or the rate of formation of the product. The rate of initiation also can be measured in the presence of small amounts of a radical inhibitor [usually used 10 mole% of di-*tert*-butylnitoxide(DTBN)] by measuring the inhibition period. The progress of the reaction can be conveniently monitored by ^{1}H NMR spectroscopy in solvents such as Me_2SO-d_6. Trial experiments for the measurement of the k.c.l. for *N*-methylmaleimide with *t*-BuHgCl/KI were not successful because of the speed of the reaction. The reaction of *N*-methylmaleimide with *t*-BuHgCl/KI in Me_2SO-d_6 goes to completion within 5 min with a sunlamp irradiation. However, with DTBN or in the dark condition the reaction retardation is observed as shown Table XXIII. Even though I could not get the exact number for k.c.l., it is apparent that the reaction possesses quite a long k.c.l..

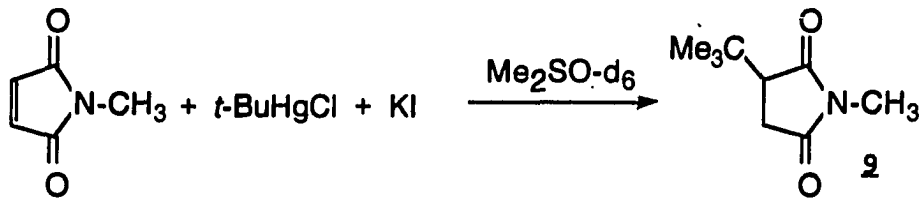
With the less reactive *t*-BuHgI, the k.c.l. of the reductive alkylation of *N*-methylmaleimide can be obtained. Without DTBN, the reaction is still so fast that it is hard to measure accurately. Two identical NMR tube reaction mixtures were prepared and analyzed alternately by ^{1}H NMR to obtain the data of Table XXIV and Fig. 3.

From Fig. 3, Initial Rate = ~0.025 M/min

Rate of Initiation = 0.00012 M/min

k.c.l. = ~200

Table XXIII. Reaction of *N*-methylmaleimide with *t*-BuHgCl/KI in Me_2SO[a]



time (min)	% of formation of 9[b]		
	no DTBN/hυ	no DTBN/dark	with DTBN/hυ[c]
0	0	0	0
5	90 - 99	0	0
10		41	0
30		53	53
40		53 (100)[d]	60
45			85
50			96
55			100

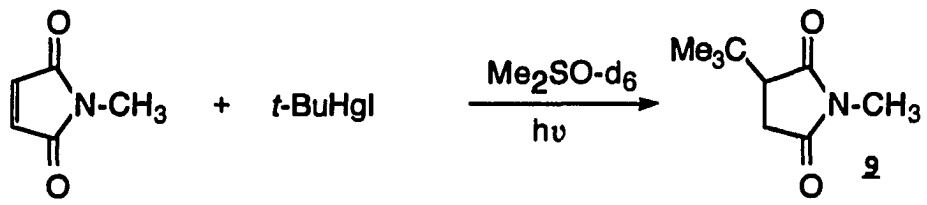
[a]*N*-Methylmaleimide (0.1 M) and *t*-BuHgCl (0.2 M), and KI (0.4 M) in 1 ml Me_2SO-d_6 was irradiated with a 275-W sunlamp at ~40 °C.

b Yields by ^1H NMR with benzene an internal standard.

[c]Yields are explained by (100 - *N*-methylmaleimide)%. Work up yield was 30%.

[d](100 - *N*-Methylmaleimide)%.

Table XXIV. Reaction of *N*-methylmaleimide with *t*-BuHgI in Me_2SO-d_6[a]



9

time (min)	% of formation of **9**[b]		
	no DTBN I	no DTBN II	with DTBN
0	0	0	0
1	26	-	-
4	-	86	-
5	87	-	-
8	-	98	-
10	100	-	-
11		100	-
75			0
90			8
120			79
135			100

[a]*N*-Methylmaleimide (0.1 M) and *t*-BuHgCl (0.2 M), and KI (0.4 M) in 1 ml Me_2SO-d_6 was irradiated with a 275-W sunlamp at ~40 °C.

[b]Yields by ^1H NMR with benzene an internal standard. Yields are explained by (100 - *N*-methylmaleimide remaining)%.

Curve A : Without DTBN

Curve B : With DTBN

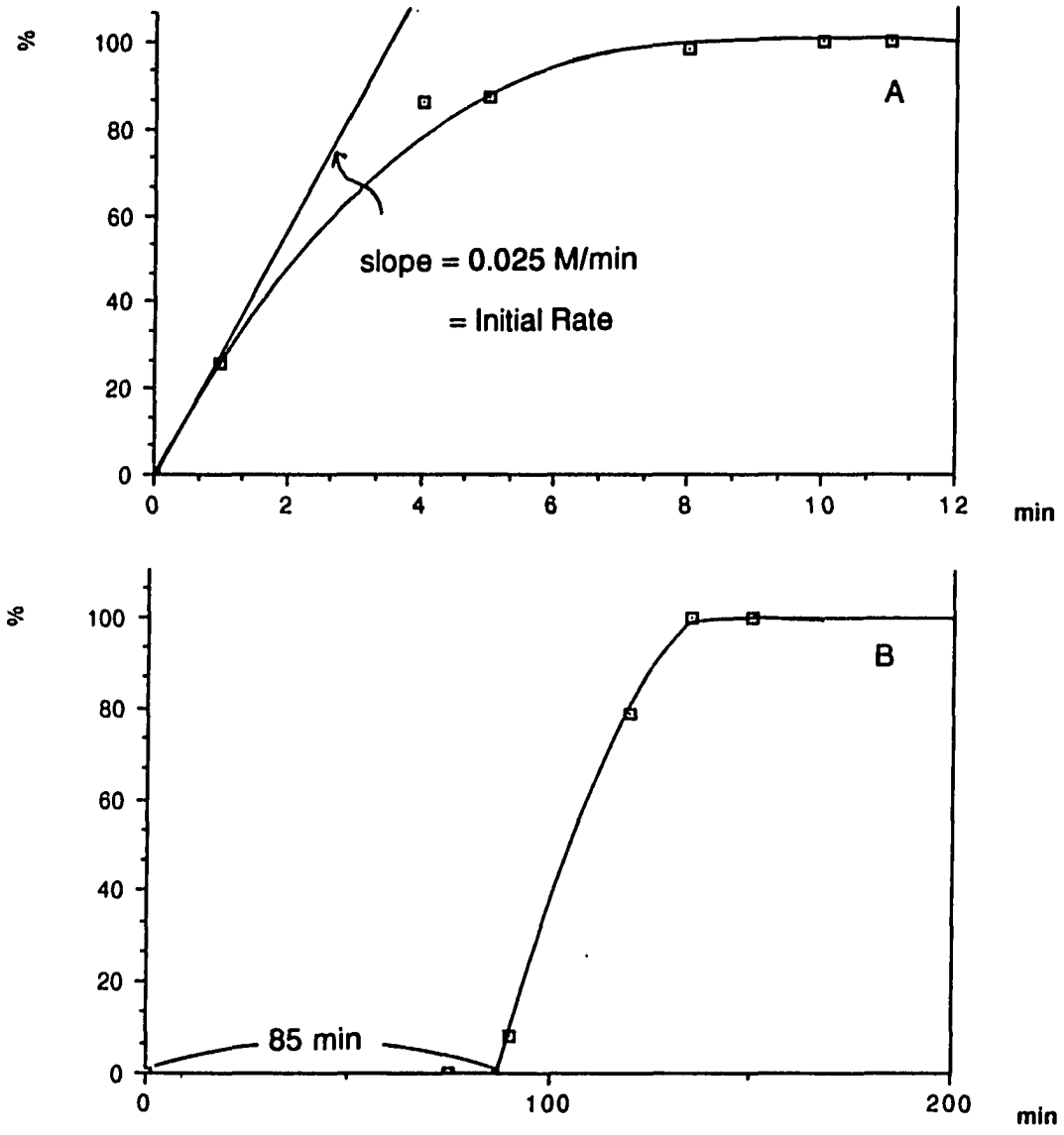


Fig. 3. Formation of product vs time for the reaction of *N*-methylmaleimide and *t*-BuHgI.

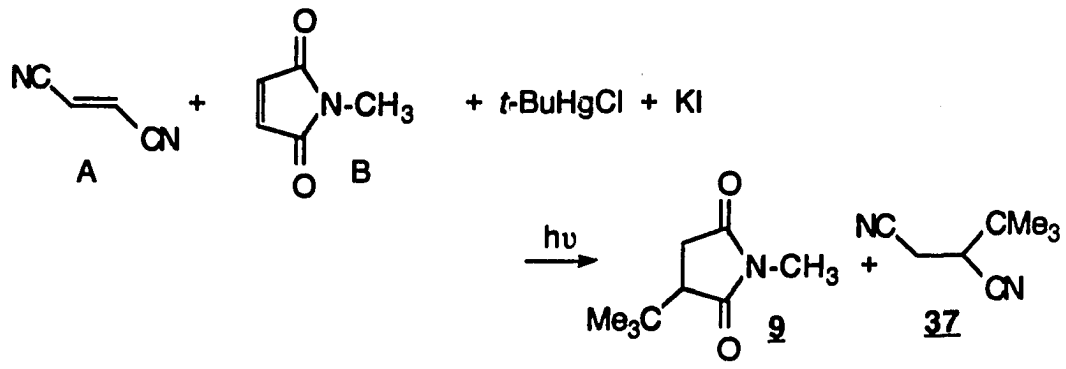
2. Relative reactivities of various compounds towards *tert*-butyl radical

Competition reactions between two substrates which individually react with *t*-BuHgCl by a chain process yield relative reactivity data concerning the product determining steps. With long kinetic chain processes, product formation in the photoinitiation or termination steps can be ignored and product formation will be determined by the irreversible addition of *t*-Bu• to the competing substrates. Most of the competition reactions were analyzed by method B (eq. 38, excess amount of *t*-BuHgCl) because method A (eq. 37, excess amount of substrate) sometimes produces unexpected coupling products of the two substrates. In most cases, β-iodostyrene was used as a standard substrate. For method A, usually 0.6 mmol of each substrate/0.25 mmol of *t*-BuHgCl/0.5 mmol of KI in Me_2SO (10 ml) were irradiated with a 275-W sunlamp at ~40 °C. For method B, 0.25 mmol of each substrate/1.0 mmol of *t*-BuHgCl/2.0 mmol of KI in Me_2SO (5 ml) were irradiated with a 275-W sunlamp at ~40 °C. Table XXV summarizes the experiments for relative reactivities of each substrate.

Among the substrates investigated, fumaronitrile is the most reactive substrate towards the *tert*-butyl radical. In general, cyano-substituted alkenes are more reactive than other substituted alkenes. *tert*-Butylation of aromatic compounds and *tert*-butylation leading to intramolecular cyclizations with aromatic rings (which will be discussed in Chapter III) gave, as expected, much lower reactivities than the *tert*-butylation of enones or enediones.

Table XXV. Relative reactivities towards *tert*-butyl radical in Me_2SO[a]

XXV-1



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] 9	% yield[b] 37	k_a/k_b
B	1 : 1 : 4 : 8	3 min	28	59	2.7
B	1 : 1 : 4 : 8	3 min	33[c]	60[c]	2.3
					Avg. 2.5 (1040)[d]

[a]Coreactants with 0.25 mmol of limiting reagent(s) in 5 ml of Me_2SO were irradiated with a 275-W sunlamp at ~40 °C.

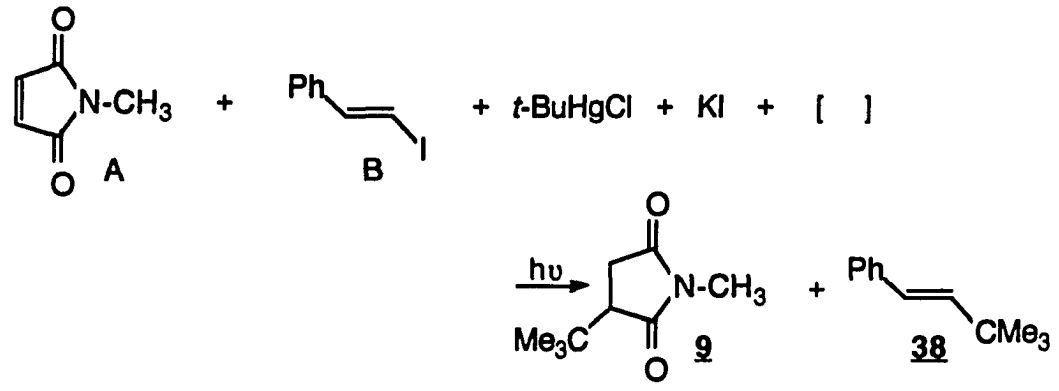
[b]GC yield with an internal standard otherwise mentioned.

[c]^1H MNR yield with benzene or toluene an internal standard after work up.

[d]Relative reactivity of the substrate A compared with β-iodostyrene.

Table XXV (continued)

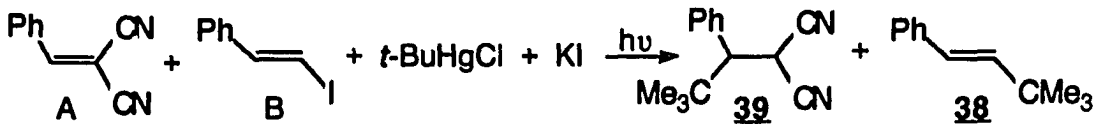
XXV-2



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] 9	% yield[b] 38	k_a/k_b
B	1 : 1 : 2 : 4	9 min	89	0.50	440
B	1 : 3 : 5 : 8	4 min	84	0.47	390
					Avg. 415
B	1 : 3 : 4 : 8 : Dabco (4)	5 - 8 min	40 - 41	0.1 - 0.2	340 - 350
					Avg. 345

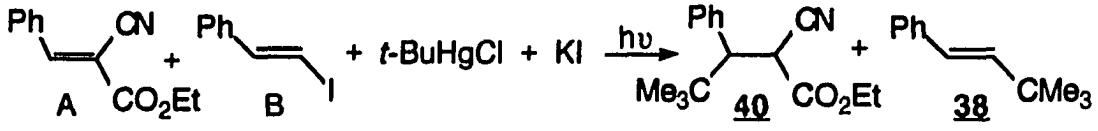
Table XXV (continued)

XXV-3



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] **39**	**38**	k_a/k_b
A	2.4 : 2.4 : 1.0 : 2.0	20 h	53	0.5	106
B	1 : 2 : 4 : 8	15 min	56	0.6	136

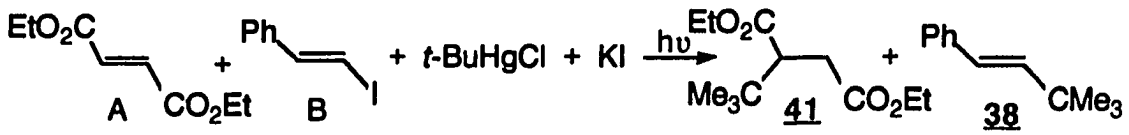
XXV-4



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] **40**	**38**	k_a/k_b
A	2.4 : 2.4 : 1.0 : 2.0	20 h	71	1.3	55
B	1 : 1 : 4 : 8	15 min	33	0.85	47

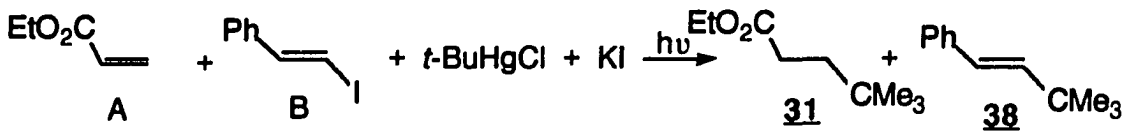
Table XXV (continued)

XXV-5



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] 41	% yield[b] 38	k_a/k_b
B	1 : 1 : 4 : 8	15 min	54[c]	2.2[c]	35

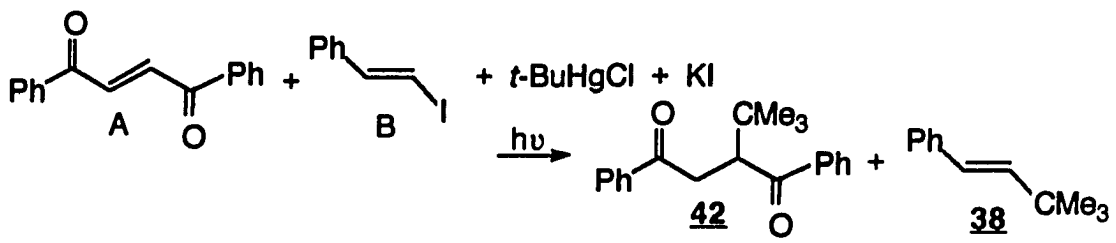
XXV-6



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] 31	% yield[b] 38	k_a/k_b
B	1 : 1 : 4 : 8	5 min	54	4.3	18
B	1 : 1 : 4 : 8	6 min	73	4.2	30
B	1 : 1 : 4 : 8	5 min	53	2.2	34
					Avg. 27

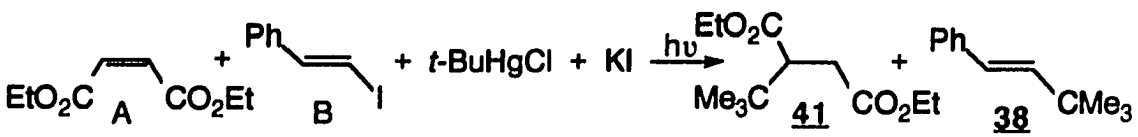
Table XXV (continued)

XXV-7



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] **42**	% yield[b] **38**	k_a/k_b
A	2.4 : 2.4 : 1.0 : 2.0	16 h	11.5	0.8	12

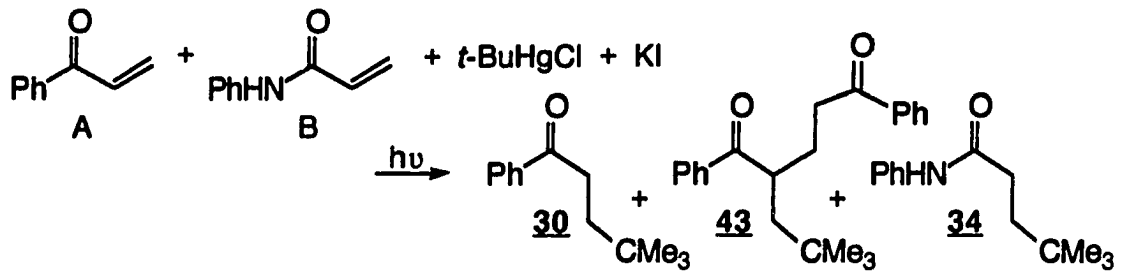
XXV-8



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] **41**	% yield[b] **38**	k_a/k_b
B	1 : 1 : 4 : 8	13 min	30[c]	3.7[c]	11
B	1 : 1 : 4 : 8	10 min	30[c]	3.6[c]	11

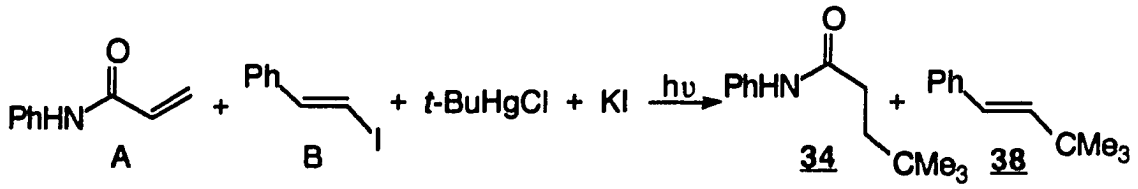
Table XXV (continued)

XXV-9



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] 30	43	34	k_a/k_b
B	1 : 1 : 4 : 8	15 min	75	7	68	1.6 (11)[d]

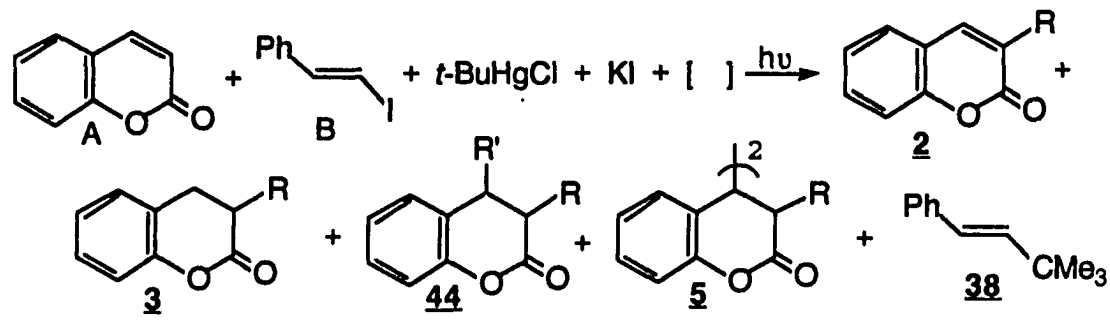
XXV-10



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] 34	38	k_a/k_b
B	1 : 1 : 4 : 8	40 min	68	37	6.8

Table XXV (continued)

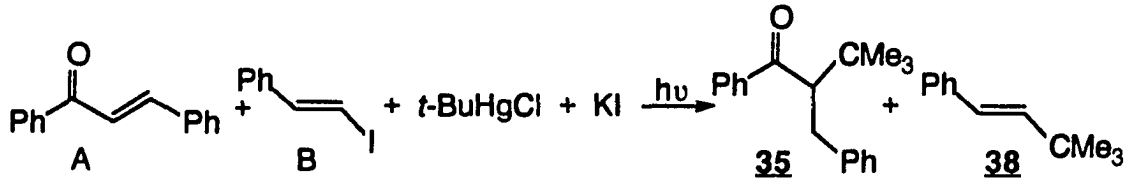
XXV-11



R = *t*-Bu, R' = CH=CHPh

method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] 2	3	44	5	38	k_a/k_b
B	1 : 1 : 4 : 8 : Dabco (2)	3 h	41	16	2	4	14	6.6
B	1 : 1 : 4 : 0 : Dabco (2)	9 h	21	2.6	1	-	4.7	6.0

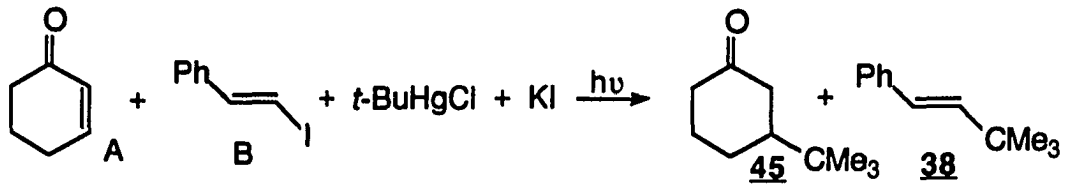
XXV-12



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] 35	38	k_a/k_b
B	1 : 1 : 4 : 4	7 h	21	4	5.8

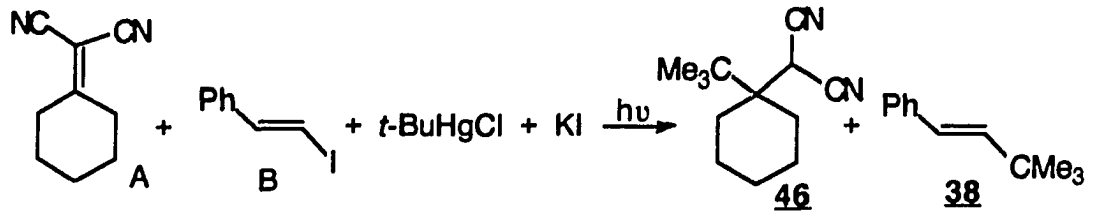
Table XXV (continued)

XXV-13



method	molar equivalents	time	% yield[b]		k_a/k_b
	A:B:*t*-BuHgCl:KI		**45**	**38**	
A	4 : 4 : 1 : 2	11 h	36	29	1.2
B	1 : 1 : 4 : 8	1 h	43	25	2.0

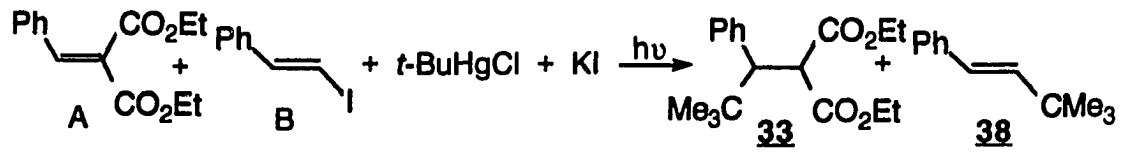
XXV-14



method	molar equivalents	time	% yield[b]		k_a/k_b
	A:B:*t*-BuHgCl:KI		**46**	**38**	
A	2.4 : 2.4 : 1 : 2	22 h	18	15	1.2
B	1 : 1 : 4 : 8	20 min	13	10	1.3

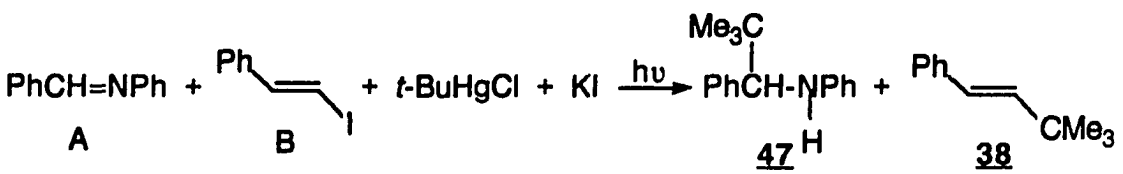
Table XXV (continued)

XXV-15



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] **46**	% yield[b] **38**	k_a/k_b
B	1 : 1 : 4 : 8	4 h	20	18	1.1

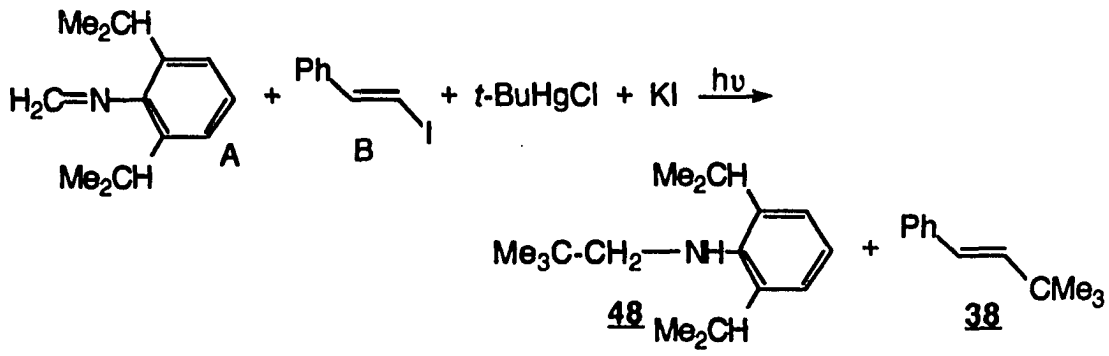
XXV-16



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] **46**	% yield[b] **38**	k_a/k_b
B	1 : 1 : 4 : 8	2.5 h	46	54	0.79

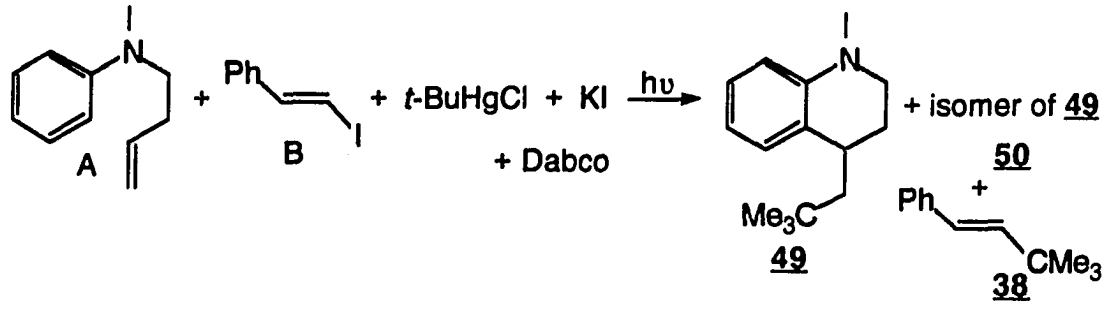
Table XXV (continued)

XXV-17



method	molar equivalents	time	% yield[b]		k_a/k_b
	A:B:*t*-BuHgCl:KI		**48**	**38**	
B	1 : 1 : 4 : 8	1.5 h	13	28	0.42

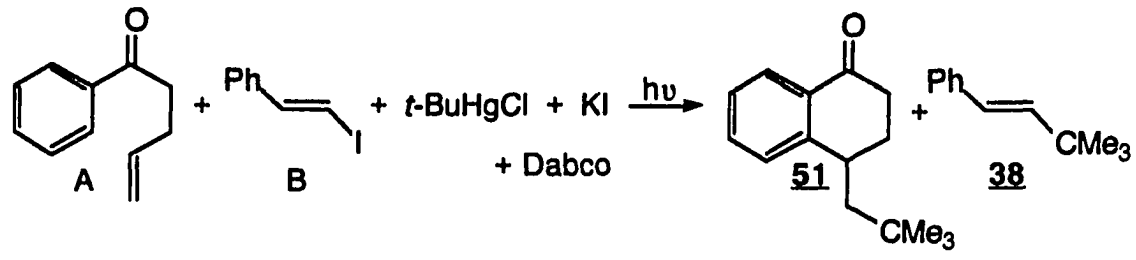
XXV-18



method	molar equivalents	time	% yield[b]			k_a/k_b
	A:B:*t*-BuHgCl:KI:Dabco		**49**	**50**	**38**	
B	1 : 1 : 4 : 8 : 4	2.5 h	5.8	2.5	71	0.074

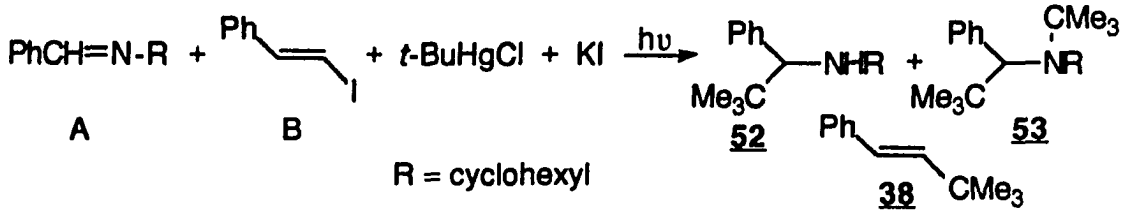
Table XXV (continued)

XXV-19



method	molar equivalents A:B:*t*-BuHgCl:KI:Dabco	time	% yield[b] 51	38	k_a/k_b
A	4 : 4 : 1 : 2 : 1	14 h	3.1	65	0.048
B	1 : 1 : 4 : 8 : 4	2.5 h	11	92	0.046

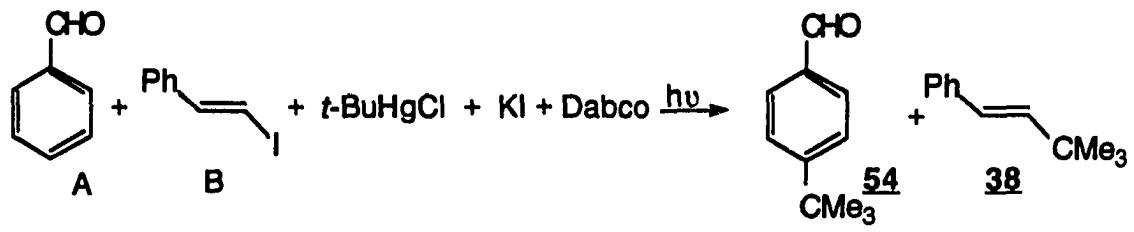
XXV-20



method	molar equivalents A:B:*t*-BuHgCl:KI	time	% yield[b] 52	53	38	k_a/k_b
B	1 : 1 : 4 : 8	1 h	1.9	0.2	50	0.031

Table XXV (continued)

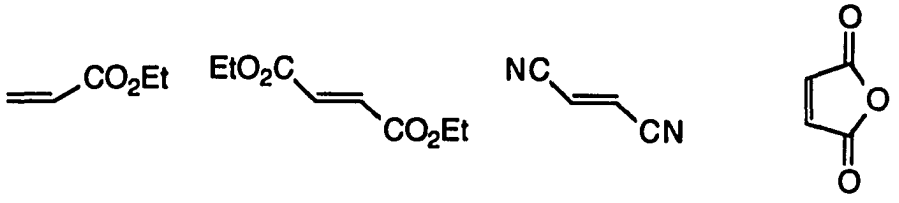
XXV-21



method	molar equivalents A:B:*t*-BuHgCl:KI:Dabco	time	% yield[b] 54	38	k_a/k_b
A	4 : 4 : 1 : 2 : 1	14 h	1.1	73	0.015

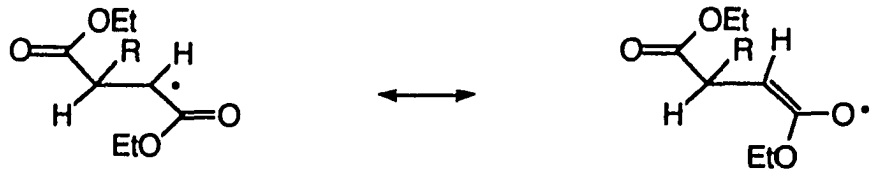
Giese[77] has reported a few relative reactivities of radical reactions with *t*-BuHgCl/$NaBH_4$. Ethyl acrylate shows some spread in the experimental data, but fumaronitrile and ethyl fumarate show a good agreement between Giese's and my results.

Relative reactivities



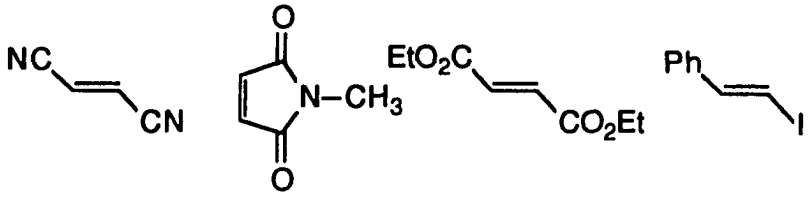
1	3.0	9.0	234	lit.[77]
2.3	3.0	10.0	-	this study

As shown Table XXV-5 and -8, trans and cis isomers of 1,2-disubstituted ethylenes have an interesting relative reactivity (ethyl maleate : ethyl fumarate = 1 : 3.2). These differences were first studied by Lewis and Mayo[78] with fumarates and maleates where in co-polymerizations the more stable fumarates were the most reactive. This result has been ascribed to steric inhibition of resonance. When a radical R• adds to these substrates, the transition state will be most stabilized by resonance if the carbonyl oxygen atom lies in the same plane as the atoms attached to the doubly bonded carbon atoms. Consideration of a model of maleic ester shows that both ester groups cannot be coplanar simultaneously, and considerable steric inhibition of resonance is involved if one assumes the a coplanar configuration is required.



In fumarate esters, on the other hand, no such interference exists. It is therefore reasonable that resonance stabilization of the transition state should be more effective in reducing the activation energy of radical addition to fumarates than maleates.

The relative reactivities in reductive and oxidative alkylations are of interest. If the products are determined only by the rate of the *t*-Bu• addition, reactivities should be independent of the product formed. Relative reactivities of the oxidative alkylation of fumaronitrile and *N*-methylmaleimide were examined by use of diethyl fumarate as a standard. Diethyl fumarate produces only the reductive alkylation product irrespective of the reaction conditions (Chapter I). As shown in Table XXVI, relative rates for the oxidative alkylation of fumaronitrile and *N*-methylmaleimide decrease by one-half compared with the reductive alkylation of each substrate.



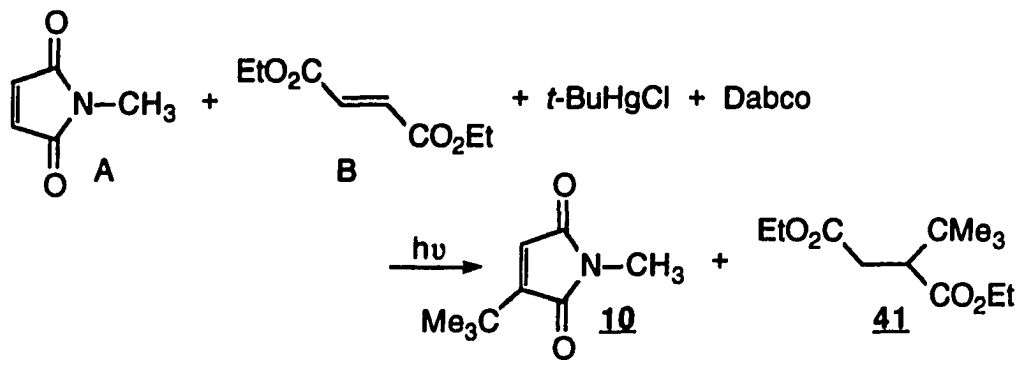
Reductive	1038	415	35	1
Oxidative	490	210		

The relative reactivities of *N*-methylmaleimide and fumaronitrile are practically constant in reductive alkylation (with KI) and oxidative alkylation (with Dabco). The reactivity of diethyl fumarate relative to either *N*-methylmaleimide or fumaronitrile seems to be higher under the oxidative alkylation conditions by a factor of ~2. The difference is not great but is in the direction expected if the

presence of KI some of diethyl fumarate product 41 was lost by conversion to the acid.

Table XXVI. Relative reactivities of *N*-methylmaleimide and fumaronitrile for oxidative alkylation in Me_2SO[a]

XXVI-1



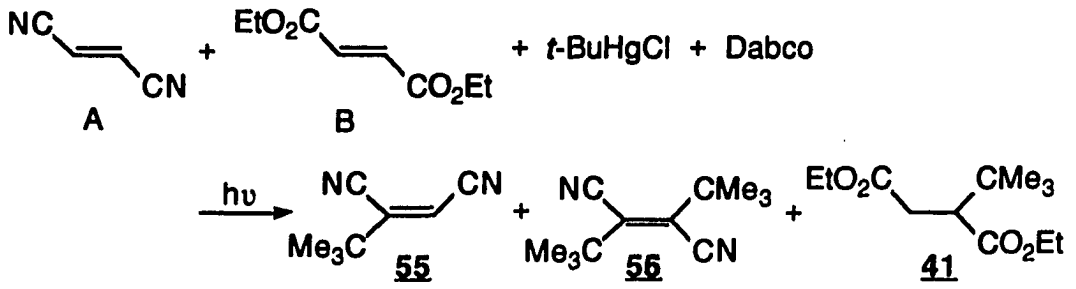
method	molar equivalents A:B:*t*-BuHgCl:Dabco	time	% yield[b] 10	% yield[b] 41	k_a/k_b
B	1 : 1 : 6 : 8	6 h	26	5	6.0
B	1 : 1 : 6 : 8	4.5 h	25	5	5.7
					Avg. 5.9

[a]Coreactants with 0.5 mmol of limiting reagent(s) in 10 ml of Me_2SO were irradiated with a 275-W sunlamp at ~40 °C.

[b]^1H NMR yield with an internal standard after work up.

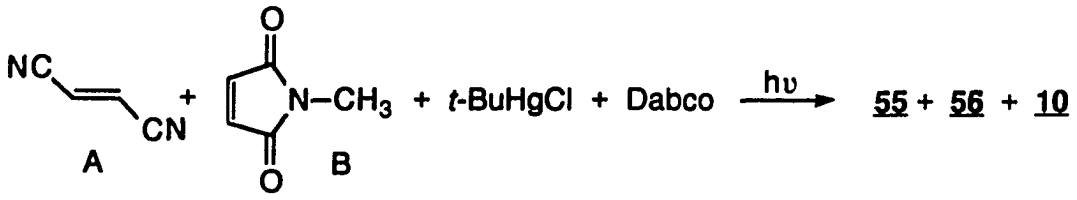
Table XXVI (continued)

XXVI-2



method	molar equivalents A:B:*t*-BuHgCl:Dabco	time	% yield[b] 55	56	41	k_a/k_b
B	1 : 1 : 6 : 6	6 h	73	3	10	14
B	1 : 1 : 6 : 8	2.5 h	47	1.6	4.7	14
						Avg. 14

XXVI-3

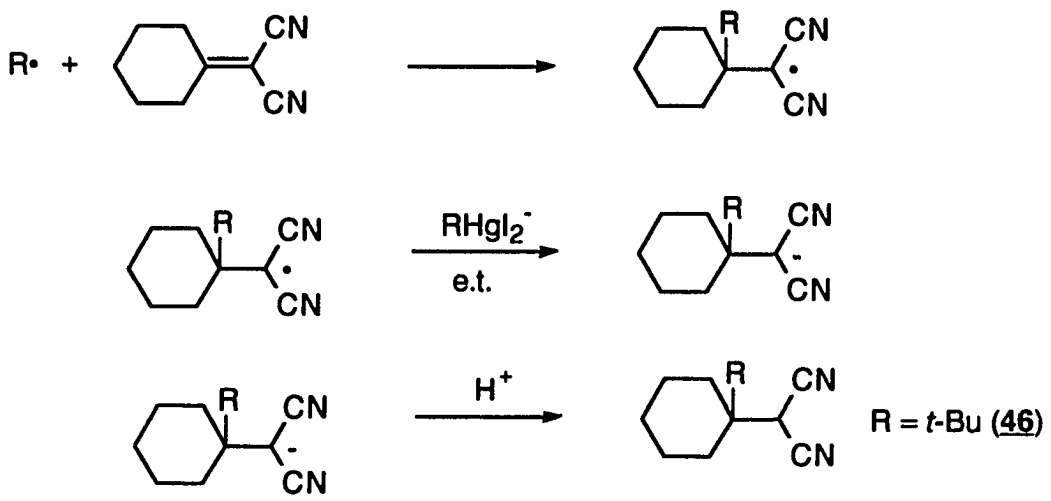


method	molar equivalents A:B:*t*-BuHgCl:Dabco	time	% yield[b] 55	56	10	k_a/k_b
B	1 : 1 : 6 : 8	4 h	23	1.4	15	1.7
B	1 : 1 : 6 : 6	6 h	20	1.8	8	2.9
B	1 : 1 : 6 : 8	4.5 h	42	0.9	26	1.9
						Avg. 2.2

3. Effects of acids or trimethylsilyl iodide (TMSI) on the alkylation of imines and α,β-unsaturated nitriles

In some cases, *tert*-butylation (in the presence of I^-) of α,β-unsaturated nitriles gives an increased yield of the reductive alkylation product in the presence of *p*-toluenesulfonic acid (PTSA).[79] Two factors may be involved. First, protonation of the substrate or the adduct radical may increase the reactivity towards *tert*-butyl radical attack or electron transfer between the adduct radical and *t*-BuHgI_2^-. Second, the anion which is generated after the electron transfer from adduct radical to *t*-BuHgI_2^-, can be protonated which can prevent the polymerization or the formation of other by-products. To examine these possibilities, relative reactivity experiments for a nitrile and an imine in the presence and absence of PTSA or TMSI were performed. As shown Table XXVII, TMSI or PTSA does not effect the relative reactivity of 1,1-dicyanomethylene-cyclohexane towards *tert*-butylation. Thus the only function of the acid is believed to transfer the proton after the adduct radical has been formed. In part this may be due to protonation of the carbanion formed by electron transfer. This would decrease the formation of by-products and produce a higher yield of the reductive alkylation product than without PTSA or TMSI (Scheme18).

Scheme 18



Another possibility is that the adduct radical from an α,β-unsaturated nitrile can itself be protonated. This would be expected to greatly increase the efficiency of electron transfer from *t*-BuHgI$_2^-$/I$^-$ (Scheme 19).

Scheme 19

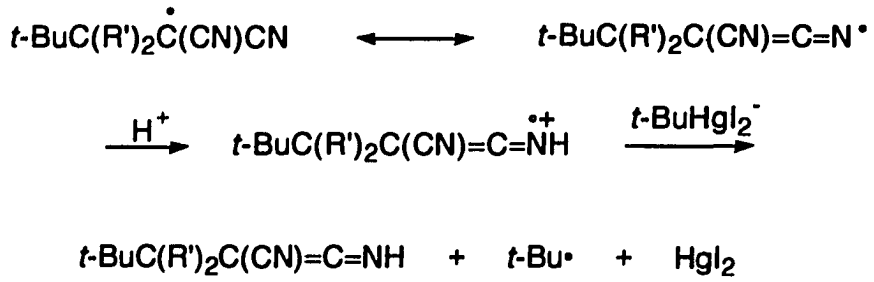
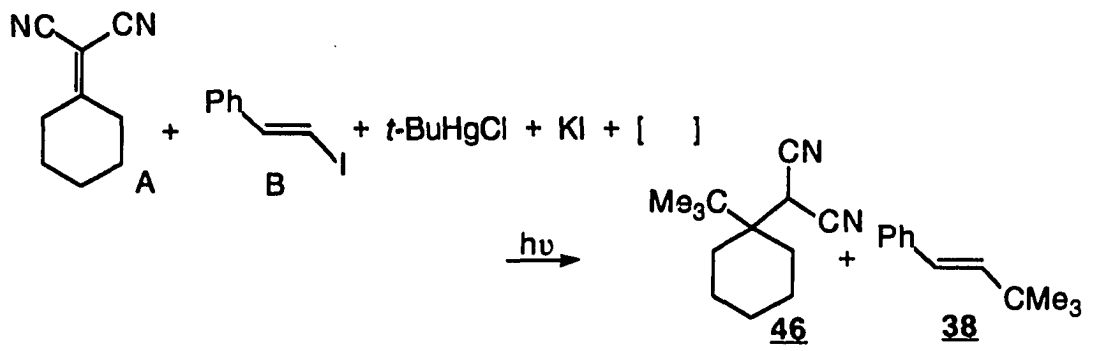


Table XXVII. Relative reactivities of 1,1-dicyano methylenecyclohexane towards *tert*-butyl radical in the presence of PTSA or TMSI in Me_2SO[a]



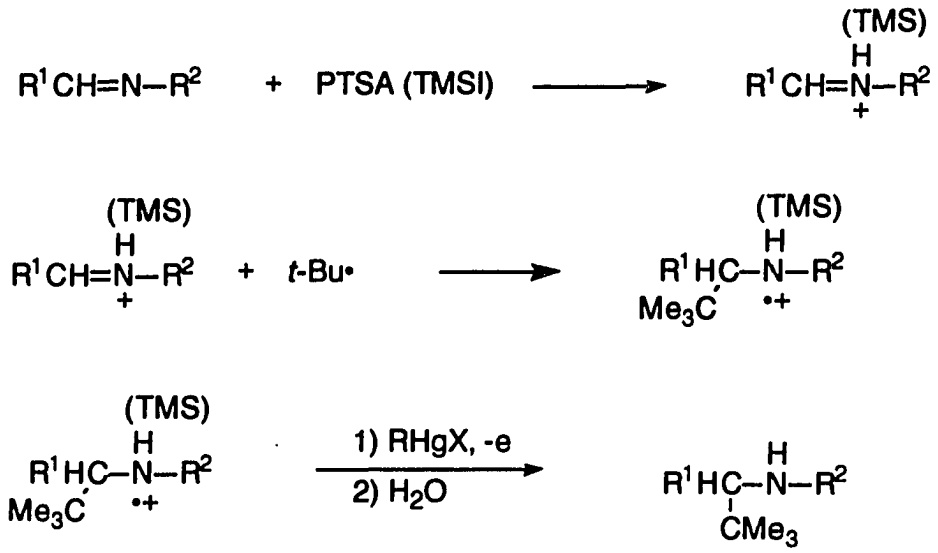
method	molar equivalents A:B:*t*-BuHgCl:KI:[ ]	time	% yield[b] 46	% yield[b] 38	k_a/k_b
B	1 : 1 : 4 : 8	20 min	13	10	1.3
B	1 : 1 : 4 : 8 : PTSA (1)	15 min	11	17	1.6
B	1 : 1 : 4 : 8 : TMSI (1)	20 min	9	11	1.2

[a]Coreactants with 0.25 mmol of each substrate in 5 ml of Me_2SO were irradiated with a 275-W sunlamp at ~40 °C.

[b]GC yield with toluene an internal standard.

However, the reactivity of imines is increased by introducing PTSA or TMSI into the reaction mixture which strongly suggest that PTSA or TMSI facilitates the *tert*-butyl radical addition to the imines as shown in Scheme 20.

Scheme 20

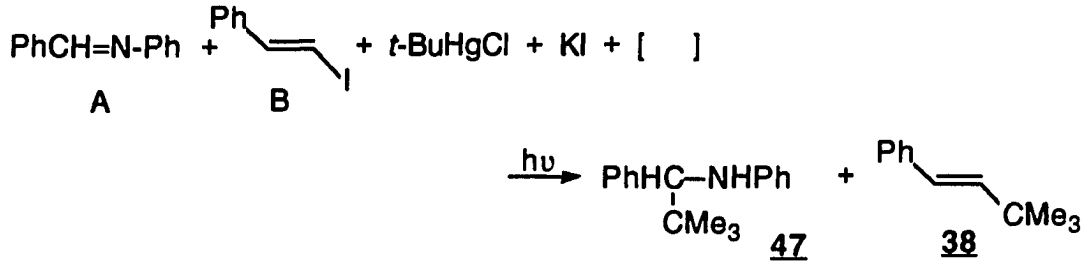


R^1 = H, Ph; R^2 = Ph, cyclohexyl, 2,6-diisopropylbenzyl

Tables XXVIII, XXIX, and XXX summarize the results. In general, PTSA and TMSI are effective in enhancing the reactivity of imines while acetic acid doesn't have an appreciable effect, presumably because of its lower acidity.

By adding PTSA (6 equiv) to the reaction mixture of PhCH=N-Ph/*t*-BuHgCl /KI/hυ in Me_2SO, the reactivity is increased by 5-fold using β-iodostyrene as a standard *t*-Bu• trapping reagent. The addition of TMSI (1 equiv) also enhances the reactivity by 3-fold. Addition of acetic acid in the reaction mixture, as mentioned above, doesn't effect for the reactivity enhancement (Tables XXVIII and XXIX).

Table XXVIII. Relative reactivity of *N*-benzylideneaniline towards *tert*-butyl radical in the presence of acids or TMSI in Me_2SO[a]

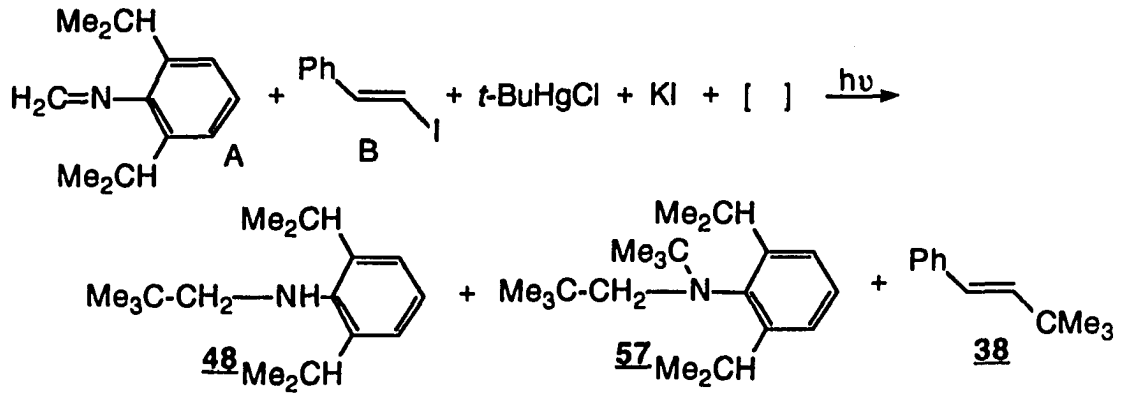


method	molar equivalents A:B:*t*-BuHgCl:KI:[ ]	time	% yield[b] 47	% yield[b] 38	k_a/k_b
B	1 : 1 : 4 : 8	2.5 h	46	54	0.79
B	1 : 1 : 4 : 8 : AcOH (0.5 ml)	40 min	32	60	0.42
B	1 : 1 : 4 : 8 : TMSI (1)	15 min	71	38	2.6
B	1 : 1 : 4 : 8 : PTSA (6)	60 min	80	33	4.0

[a]Coreactants with 0.25 mmol of each substrate in 5 ml of Me_2SO were irradiated with a 275-W sunlamp at ~40 °C.

[b]GC yield with toluene as an internal standard.

Table XXIX. Relative reactivity of *N*-methylene-2,6-diisopropylaniline towards *tert*-butyl radical In the presence of acids or TMSI in Me_2SO[a]

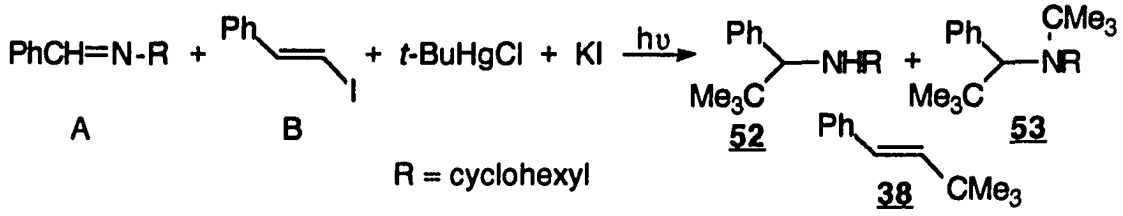


method	molar equivalents A:B:*t*-BuHgCl:KI:[ ]	time	% yield[b] 48	57	38	k_a/k_b
B	1 : 1 : 4 : 8	90 min	13	-	28	0.42
B	1 : 1 : 4 : 8 : AcOH (0.5 ml)	20 min	14	1.5	19	0.82
B	1 : 1 : 4 : 8 : TMSI (1)	15 min	54	11	15	6.4
B	1 : 1 : 4 : 8 : PTSA (3)	15 min	44	14	11	7.4

[a]Coreactants with 0.25 mmol of each substrate in 5 ml of Me_2SO were irradiated with a 275-W sunlamp at ~40 °C.

[b]GC yield with toluene an internal standard.

Table XXX. Relative reactivity of *N*-benzylidenecyclohexylamine towards *tert*-butyl radical in the presence of acids or TMSI in Me_2SO[a]



A B R = cyclohexyl **52** **53** **38**

method	molar equivalents A:B:*t*-BuHgCl:KI:[ ]	time	% yield[b] **52**	**53**	**38**	k_a/k_b
B	1 : 1 : 4 : 8	60 min	1.9	0.2	50	0.031
B	1 : 1 : 4 : 8 : TMSI (1)	20 min	36	5.4	5.9	8.8
B	1 : 1 : 4 : 8 : PTSA (3)	20 min	57	7.9	7.9	12.7

[a]Coreactants with 0.25 mmol of each substrate in 5 ml of Me_2SO were irradiated with a 275-W sunlamp at ~40 °C.

[b]GC yield with toluene an internal standard.

N-Methylene-2,6-diisopropylaniline shows a similar reactivity sequence. PTSA (3 equiv) enhances the reactivity by 18-fold and TMSI (1 equiv) by 15-fold. Again, acetic acid shows a little effect. *N*-benzylidenecyclohexylamine, which has a more basic lone pair of electrons on nitrogen, shows a much large effect when PTSA (3 equiv) or TMSI (1 equiv) is introduced in the reaction mixture. PTSA increases the reactivity 410-fold and TMSI by 280-fold.

Pyridine undergoes photostimulated ring substitution with a variety of alkylmercury halides. When an excess of pyridine is used as the solvent, ortho and para (ortho > para) alkylated products are observed.[24] For the relative reactivity experiment, Me_2SO was used as the solvent as usual even though reactions are complicated by the formation of dialkylated pyridine. Again, the reactivities with *t*-BuHgCl/KI relative to (*E*)-PhCH=CHI increase upon conversion of pyridine to pyridinium ion. As shown in Table XXXI, the reactivity of pyridine increases upon protonation or silylation from 0.53 to 4.9 (PTSA), 12 (CF_3CO_2H), and 1.6 (TMSI). The reactivity of pyridinium ion (PyH^+) towards *t*-Bu• is believed to be 1000 times greater than that of pyridine (Py) towards *t*-Bu•.[80] Compared with this known value, the effectiveness of acids or TMSI is somewhat less than expected and *t*-BuHgCl itself seems to play a role in increasing the reactivity. In other words, complexation between *t*-BuHgCl and pyridine which forms $Py^{\delta+}\cdots Hg^{\delta-}$(*t*-Bu)Cl complex. With an excess (12 equiv) of Dabco, the reactivity decreases from 0.53 to ~0.003 which strongly suggests that promotion of the radical addition reaction by pyridine····*t*-BuHgCl complexation. Thus, for pyridine/*t*-BuHgCl/KI reactions, not only acids or TMSI, but also *t*-BuHgCl complexation with pyridine increases the reactivity towards *t*-Bu•.

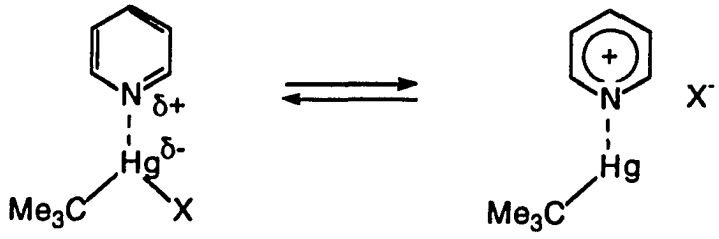
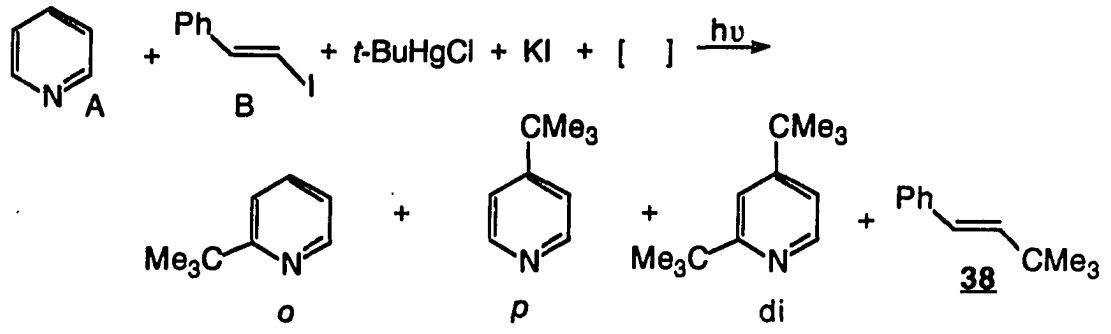


Table XXX. Relative reactivity of pyridine towards *tert*-butyl radical in the presence of acids or TMSI in Me_2SO[a]



method	molar equivalents A:B:*t*-BuHgCl:KI:[ ]	time	% yield[b] *o*	*p*	di	**38**	k_a/k_b
B	1 : 1 : 4 : 8	20 min	8	7	1	28	0.53
B	1 : 1 : 4 : 8 : TMSI (1)	20 min	18	10	9	25	1.6
B	1 : 1 : 4 : 8 : PTSA (2)	20 min	31	14	10	15	4.9
B	1 : 1 : 4 : 8 : CF_3CO_2H (3)	20 min	33	21	18	10	12
B	1 : 1 : 4 : 8 : Dabco (12)	120 min	(0.2 - 0.3)[c]			57	~0.003

[a]Coreactants with 0.25 mmol of each substrate in 5 ml of Me_2SO were irradiated with a 275-W sunlamp at ~40 °C.

[b]^1H NMR yield with toluene as an internal standard after work up.

[c]Total amounts of alkylated pyridines.

D. Conclusion

The measures initial kinetic chain length for the reaction of *t*-BuHgI with *N*-methylmaleimide is ~200. The relative reactivities of α,β-unsaturated carbonyls, 1,4-enediones, α,β-unsaturated nitriles, imines, *N*-but-3-enyl-*N*-methylamino-benzene, and aromatic carbonyls towards *tert*-butyl radical attack have been determined and are summarized in Table XXXI using β-iodostyrene as the standard *t*-Bu• trap. The reactivity of imines towards *tert*-butyl radical is increased by introducing PTSA or TMSI in the reaction mixture.

Table XXXI. Relative reactivities towards *tert*-butyl radical compared with β-iodostyrene by using method B

compound	Rel. react.
Fumaronitrile (reductive)	1040
Fumaronitrile (oxidative)	490
N-Methylmaleimide (reductive)	415
N-Methylmaleimide (oxidative)	210
Benzylidenemalononitrile	136 (106)[a]
trans-Ethyl α-cyanocinnamate	47 (55)[a]
Ethyl fumarate	35
Ethyl acrylate	27
Dibenzoyl ethylene	12
Ethyl maleate	11

[a]By using method A.

Table XXXI (continued)

compound	Rel. react.
Phenyl vinyl ketone	11
N-Phenyl-2-propenamide	6.8
Coumarin	6.6 (6.0)[b]
Chalcone	5.8
Cyclohexenone	2.0 (1.2)[a]
Cyclohexylidene malononitrile	1.3 (1.2)[a]
Diethyl phenylmethylenemalononitrile	1.1
N-Benzylideneaniline	0.79
N-methylene-2,6-diisopropylaniline	0.42
N-But-3-enyl-*N*-methylaminobenzene	0.074
1-Phenyl-4-penten-1-one	0.046 (0.048)[a]
N-Benzylidenecyclohexylamine	0.031
Benzaldehyde	0.015

[b]Without KI.

E. Experimental Section

1. General consideration

^{1}H NMR spectra were recorded on a 300 MHz Nicolet NT300 spectrometer. Product yields were determined by integration of the ^{1}H NMR spectrum with a known amount (0.5 equiv) of benzene or toluene as an internal standard, or by gas chromatographic analysis performed on a Varian 3700 Gas

Chromatograph with a packed chromosorb W (80 - 100 mesh) column coated with 7% OV-3 and a thermal conductivity detector. Products yields by GC analysis were determined by addition of a known amount of toluene as an internal standard. *tert*-Butylmercury halides were 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 the reductive alkylation of *N*-methylmaleimide

N-Methylmaleimde (0.2 mmol), *t*-BuHgX (0.4 mmol), and with or without KI (0.8 mmol) were dissolved in 2 ml of nitrogen-purged deutrated Me_2SO in the dark. Benzene (0.1 mmol) as an internal standard was introduced into the solution. The solution was divided into two NMR tubes (1 ml in each tube) which equipped with rubber septa. After a ^1H NMR spectrum of initial solution was obtained, the reaction mixture was irradiated with a 275-W GE sunlamp ca. 25 cm from the reaction tube. The progress of the reaction was monitored at different periods of time by ^1H NMR integration of protons. The reaction in the presence of 10 mol% of DTBN was carried out under the same conditions. The yields of the product at different time are listed in Tables XXIII and XXIV.

3. Preparation of β-iodostyrene[81]

Phenylacetylene (50 mmol) and catecholborane (50 mmol) were stirred in a 100 ml flask for 2 hours under nitrogen at 70 ^oC 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 boric 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 destroyed 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; ^1H 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 ^1H NMR spectrum agreed with literature values.[81]

4. <u>General procedure for the competition reactions</u>

For method A, the substrate (0.6 mmol), β-iodostyrene (0.6 mmol), *t*-BuHgX (0.25 mmol), KI (0.5 mmol) with or without Dabco were dissolved in 5 ml of deoxygenated Me_2SO in a pyrex tube equipped with a rubber septum. After photolysis, the mixture was quenched with aqueous sodium thiosulfate solution and extracted with ether. The ether extract was washed three times with aqueous sodium thiosulfate solution, dried over $MgSO_4$, and the solvent evaporated. The GC or ^1H NMR yields were determined with toluene (0.5 equiv) or benzene (0.5 equiv) as an internal standard.

For method B, the substrate (0.25 mmol), β-iodostyrene (0.25 mmol), *t*-BuHgX (1.0 mmol), KI (2.0 mmol) with or without Dabco (0.25 - 1.0 mmol) were

dissolved in 5 ml of deoxygenated Me_2SO in a pyrex tube equipped with a rubber septum. The mixture was quenched with aqueous sodium thiosulfate solution before the reaction was completed and extracted with ether. The ether extract was washed three times with aqueous sodium thiosulfate solution, dried over $MgSO_4$, and the solvent evaporated. The GC or ^1H NMR yields were determined with toluene (0.5 equiv) or benzene (0.5 equiv) as an internal standard.

a. α-(1,1-Dimethylethyl)-succinonitrile (37)[77] The compound was identified by ^1H NMR and GCMS, and confirmed by comparison of spectral data in the literature;[77] ^1H NMR ($CDCl_3$) δ 1.13 (s, 9H), 2.79 - 2.58 (m, 3H); GCMS m/z (relative intensity) 135 (M^+ - 1, 0.1), 121 (21), 94 (28), 80 (8), 67 (17), 57 (100), 53 (11), 41 (47).

b. (*E*)-3,3-Dimethyl-1-phenylpropene (38)[81] The compound was identified by ^1H NMR and confirmed by comparison of spectral data in the literature;[81] ^1H NMR ($CDCl_3$) δ 1.12 (s, 9H), 6.24 (d,1H, J = 16.2 Hz), 6.31 (d, 1H, J = 16.2 Hz), 7.12 - 7.39 (m, 5H).

c. (2,2-Dimethyl-1-phenylpropyl)malononitrile (39)[82] The compound had ^1H NMR ($CDCl_3$) δ 1.08 (s, 9H), 3.00 (d, 1H, J = 5.7 Hz), 4.22 (d, 1H, J = 5.7 Hz), 7.38 (broad s, 5H); GCMS m/z (relative intensity) 212 (M^+, 7), 197 (3), 156 (1), 132 (6), 105 (2), 91 (7), 77 (4), 57 (100); HRMS cald for $C_{14}H_{16}N_2$ 212.1314, found 212.1315.

d. Ethyl (2,2-Dimethylethyl-1-phenylpropyl)cyanoacetate (40)[82] The compound was identified as a mixture of 2 diastereoisomers which showed one peak by GC and was not separable by flash column chromatography. ^1H NMR indicated a mixture of 2 isomers (~3 : 1); ^1H NMR ($CDCl_3$) δ 0.98 (t, J = 7.2 Hz) 1.09 (s), 1.06 (s), 3.14 (d, J = 5.1 Hz), 3.29 (d, J = 9.0 Hz), 3.85 (d, J = 9.0

Hz), 3.90 - 4.05 (m), 7.16 - 7.42 (m); GCMS m/z (relative intensity) 259 (9), 203 (8), 176 (24), 148 (5), 130 (25), 91 (21), 77 (5), 57 (100); HRMS m/z cald for 259.1572, found 259.1573.

e. 1,3-Dibenzoyl-5,5-dimethylhexane (43) The telomer was identified by GCMS only; GCMS m/z (relative intensity) 322 (M^+, 0.2), 265 (5), 224(5), 187 (4), 105 (100), 77 (27).

f. 3-(1,1-Dimethylethyl)-4-(2-phenylethenyl)-dihydrocoumarin (44) The compound was identified by GCMS only; GCMS m/z (relative intensity) 306 (M^+, 12), 250 (100), 207 (96), 178 (18), 131 (88), 115 (35), 91 (33), 83 (42), 57 (87), 41 (73).

g. 3-(1,1-Dimethylethyl)cyclohexanone (45)[83] The compound was identified by GC, GCMS, and ^1H NMR and confirmed by comparision of spectral data in literature;[83] ^1H NMR ($CDCl_3$) δ 0.85 (s, 9H), 1.30 - 1.82 (m, 5H), 2.10 - 2.40 (m, 4H); GCMS m/z (relative intensity) 154 (M^+, 32), 98 (85), 97 (30), 83 (30), 57 (100), 41 (61).

h. 1-(1,1-Dimethylethyl)cyclohexyl]malononitrile (46)[84] The compound had ^1H NMR ($CDCl_3$) δ 1.14 (s, 9H), 1.22 - 1.92 (m, 10H), 4.29 (s, 1H); GCMS m/z (relative intensity) 189 (M^+ - 14, 0.8), 148 (0.4), 121 (3), 81 (2), 67 (2), 57 (100); HRMS m/z cald for $C_{13}H_{19}N_2$ 203.1548, found 203.1551. m/z cald for $C_{12}H_{17}N_2$ 189.1392, found 189.1395.

i. *N*-(2,2-Dimethyl-1-phenylpropyl)aniline (47)[84] The compound had ^1H NMR ($CDCl_3$) δ 1.00 (s, 9H), 4.03 (s, 1H), 4.25 (s, 1H), 6.48 (d, 2H, J = 7.8 Hz), 6.57 (t, 1H, J = 7.2 Hz), 7.01 (t, 2H, J = 7.8 Hz), 7.15 - 7.30 (m, 5H); GCMS m/z (relative intensity) 239 (M^+, 4), 182 (100), 104 (10), 77 (19), 57 (1), 41 (3); HRMS cald for $C_{17}H_{21}N$ 239.1674, found 239.1678.

j. 2,6-Diisopropyl-*N*-(2,2-dimethylpropyl)aniline (48)[84] The compound had ^{1}H NMR ($CDCl_3$) δ 1.06(s, 9H), 1.24 (d, 12H, J = 6.9 Hz), 2.59 (s, 2H), 2.87 (bd s, 1H), 3.27 (sept., 2H, J = 6.9 Hz), 7.03 - 7.11 (m, 3H); GCMS m/z (relative intensity) 247 (M^+, 18), 232 (4),, 191 (20), 190 (20), 175 (24), 166 (19), 132 (10), 117 (6), 57 (6), 43 (22); HRMS m/z cald for $C_{17}H_{29}N$ 247.2301 found, 247.2301.

k. 50, isomer of 4-(2,2-dimethylethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (49) identified by GC and GCMS only; GCMS (relative intensity) 217 (M^+, 15), 202 (2), 160 (16), 120 (18), 107 (100), 77 (14), 57 (16).

l. *N*-cyclohexyl-*N*-(2,2-dimethyl-1-phenylpropyl)amine (52)[84] The compound had ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 9H), 1.03 - 1.69 (m, 10H), 1.91 (m, 1H), 2.03 - 2.17 (m, 1H), 3.43 (s, 1H), 7.18 - 7.29 (m, 5H); GCMS m/z (relative intensity) 245 (M^+, 0.02), 188 (100), 106 (88), 105 (10), 91 (15), 41 (18); HRMS m/z cald for $C_{17}H_{26}N$ (M^+ - 1) 244.2065, found 244.2067. Cald for $C_{16}H_{24}N$ (M^+ - CH_3) 230.1909, found 230.1905.

m. *N*-cyclohexyl-*N*-(1,1-dimethylethyl)-2,2-dimethyl-1-phenylpropylamine (53) The compound had was identified GCMS only; GCMS m/z (relative intensity) 302 (M^+ + 1, 0.1), 244 (100), 245 (18), 162 (51), 147 (13), 57 (17), 41 (20).

n. α-(1,1-Dimethylethyl)malenonitrile (55)[84] The compound had ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 9H), 5.91 (s, 1H); GCMS m/z (relative intensity) 134 (M^+, 4), 119 (100), 107 (30), 92 (65), 65 (37), 57 (57); HRMS m/z cald for $C_8H_{10}N_2$ 134.0844, found 134.0844.

o. **α,α'-Bis(1,1-dimethylethyl)fumaronitrile (56)**[84] The compound had ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 18H); GCMS m/z (relative intensity) 190 (M^+, 0.4), 175 (5), 134 (10), 95 (11), 57 (100).

p. **2,6-Diisoproyl-*N*-(2,2-dimethylethyl)-*N*-(2,2-dimethylpropyl)-aniline (57)** The compound had was indentified by GCMS only; GCMS m/z (relative intensity) 303 (M^+, 14), 246 (100), 247 (20), 216 (19), 57 (6), 43 (8).

tert-Butylated pyridine products were identified by comparison of ^{1}H NMR (Me_2SO-d_6) of the authentic samples. Spectral data for **2**, **3**, **5**, **9**, **30**, **31**, **33**, **34**, **35**, **41**, and **42** were presented in Chapter I and spectral data of **49**, **51**, and **53** will be presented in Chapter III.

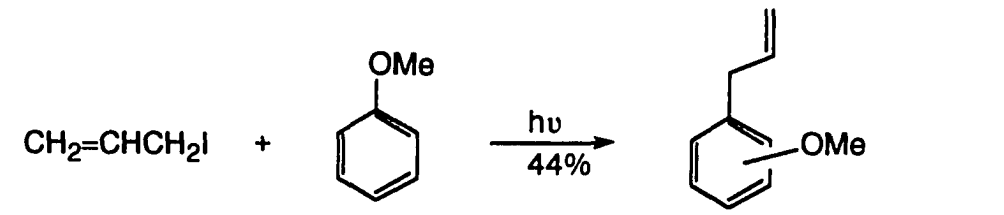
III. ALKYLATIONS OF AROMATIC COMPOUNDS AND CYCLIZATION REACTIONS VIA FREE RADICAL CHAIN REACTIONS

A. Introduction

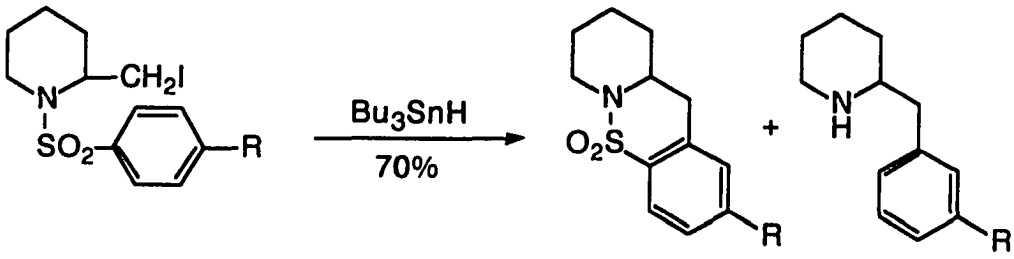
Substitution reactions of aromatic compounds in which the attacking species is a radical have been studied by Hey and co-workers. The first clear piece of evidence for the presence of reactive radicals in solution was obtained by Hey in 1934 in a study of the decomposition of diazonium salts in a variety of aromatic solvents.[85] Hey observed that the *para*-substituted biaryl, among other substitution products, was always observed irrespective of the electronic characteristic of the substituent already present in the aromatic compound. This is in marked contrast to the effects of substituents in aromatic nitration. It was account for these and other anomalies that Hey and Waters[6] in 1937 proposed the idea of short-lived neutral free radicals.

Arylation via homolytic aromatic substitution reactions has been developed because of the considerable synthetic utility.[1] Homolytic alkylation of aromatic substrates has been studied in far less detail than arylation. The methylation of a wide range of aromatic compounds has, however, been studied, but mainly from the point of correlating the reactivity with theoretical parameters. Benzene behaves like an electron-rich alkene and is attacked by nucleophilic alkyl radicals with rate coefficients of 10 - 10^3 l/mol•s at 25 - 80 ^{o}C.[86,87] This is slightly slower than the addition to alkylated alkenes[14,87] and is hardly fast enough for synthetic applications involving a chain reaction (for chain reactions to occur the

propagation steps require constants greater than 10^2 l/mol•s).[13] Thus nucleophilic π radicals such as $R_3C^•$ give rise to substitution products only if the aromatic compounds are substituted with electron-withdrawing groups or if electron-poor heterocyclic salts are used. Synthetic applications with benzoid compounds are rare because addition rates and position selectivities are low. Therefore, only a few synthetically interesting cases exist in which alkyl radicals of this type, generated from for example iodides, react with benzoid systems.[88,89]



o : *m* : *p* = 48 : 16 : 46



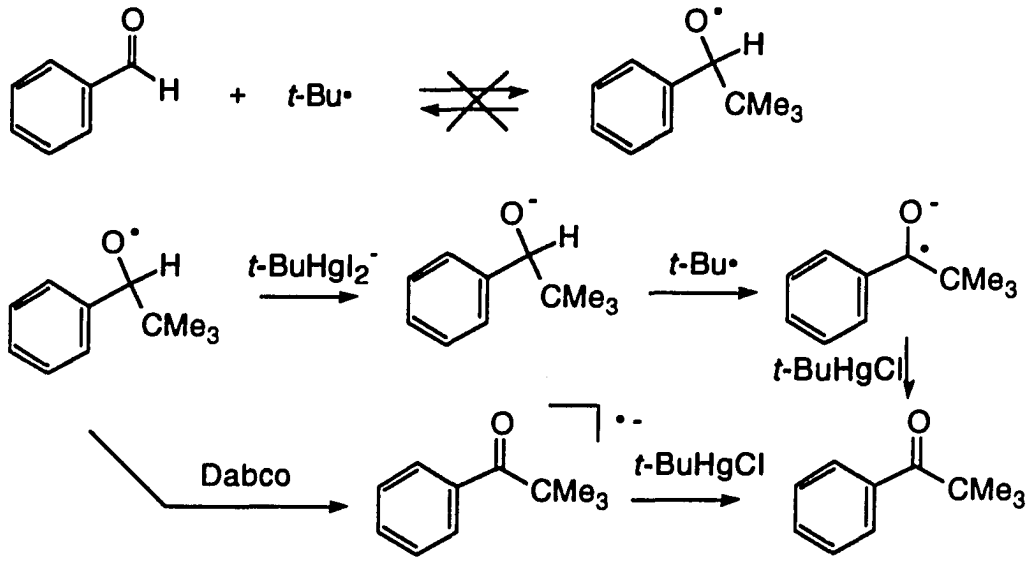
In this Chapter, alkylations of electron-deficient aromatic compounds and intramolecular cyclization reactions via free radical reactions will be presented by using the technique of oxidative alkylation which was discussed in Chapter I.

B. Results and Discussion

1. *para*-Alkylation of aromatic compounds via photostimulated radical chain reactions

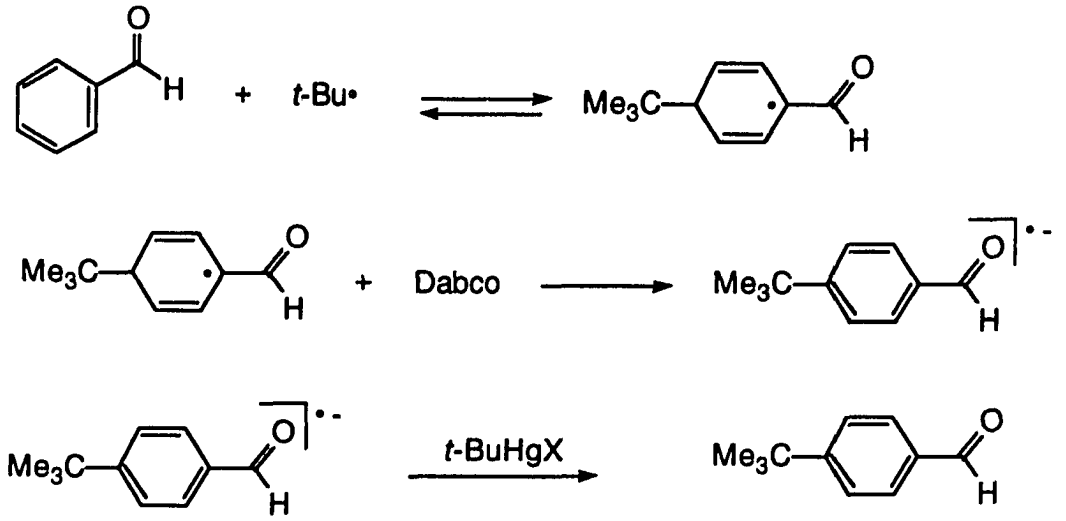
Addition of alkyl radical to monosubstituted aromatic compounds usually produces a mixture of ortho, meta, para substituted products and addition rates are low as mentioned in the introduction. Trial experiments for the alkylation of benzaldehyde with *t*-BuHgCl, *t*-BuHgCl/KI, or *t*-BuHgCl/KI/$K_2S_2O_8$ failed. However, by introducing Dabco into the reaction mixture, alkylation of the aromatic ring is observed. Radical attack at the carbonyl group is not observed under any conditions (Scheme 21).

Scheme 21



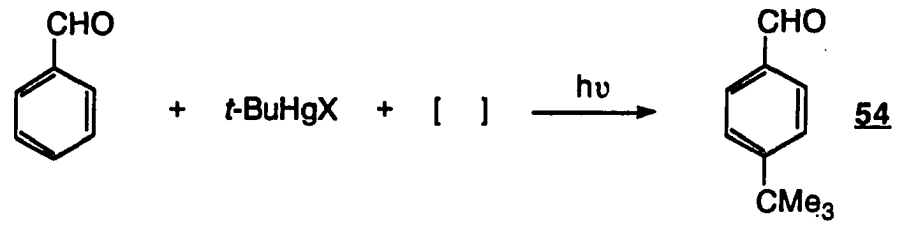
The *tert*-butyl radical attacks the aromatic ring in the para position exclusively. Apparently an electron-withdrawing group (-CHO) promotes the radical alkylation by activating the aromatic ring for nucleophilic radical attack. Exclusive product of *para*-alkylation is somewhat unexpected. It may be that *t*-Bu• addition is reversible and steric effect favors para position. The reaction of benzaldehyde with *t*-BuHgX to form *p-tert*-butylbenzaldehyde in the presence of Dabco apparently involved the removal of a proton (Schme 22) by a mechanism which is similar to the oxidative alkylation described previously.

Scheme 22



The results are summarized in Table XXXII and with *t*-BuHgI (6 equiv)/Dabco (4 equiv) the best yield (60%) is observed. Bases such as KOH or *t*-BuOK are not as good as Dabco and with these bases the reaction produces only a lot of trace products.

Table XXXII. Photostimulated reactions of benzaldehyde with *t*-BuHgX in Me_2SO[a]



54

X	molar equivalents *t*-BuHgX:KI:$K_2S_2O_8$:Dabco	time (h)	% yield of 54[b]
Cl	4 : 0 : 0 : 0	24	3[c]
Cl	4 : 4: 0 : 0	24	-
Cl	4 : 4: 2 : 0	24	4
Cl	4 : 0: 0 : 4	21	43[c]
Cl	8 : 0: 0 : 4	24	52[c]
Cl	4 : 4: 0 : 4	21	20[c]
I	4 : 0 : 0 : 4	42	48[c]
I	6 : 0 : 0 : 6	42	53[c]
I	6 : 0 : 0 : 4	42	60[c]

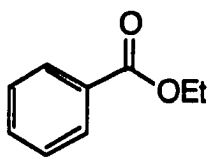
[a]0.5 Mmol of benzaldehyde in 10 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]By GC with toluene as an internal standard.

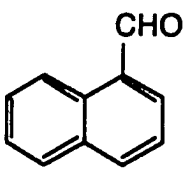
[c]Unreacted benzaldehyde remained.

The more reactive and less sterically hindered isopropyl radical with benzaldehyde produces the mixture of ortho, meta, and para (34%) alkylation products and some of the diisopropyl-substituted benzaldehyde. Substitutive alkylation of *p*-chlorobenzaldehyde with *t*-BuHgCl, *t*-BuHgCl/KI, or *t*-BuHgCl/KI/$K_2S_2O_8$ was not successful and starting *p*-chlorobenzaldehyde was recovered after the work up.

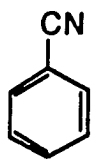
Photostimulated reaction of acetophenone, benzophenone, and the *tert*-butyl phenyl ketone showed also exclusive *para*-alkylation product with the *tert*-butyl radical/Dabco system (Tables XXXIII, XXXIV, XXXV). However, the following compounds gave poor results.



; 10% of para *tert*-butylation with *t*-BuHgI (6 equiv)/Dabco (4 equiv)/Me_2SO (42 h).



; 18% of para *tert*-butylation with *t*-BuHgI (6 equiv)/Dabco (4 equiv)/Me_2SO (46 h).



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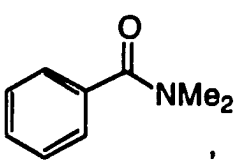

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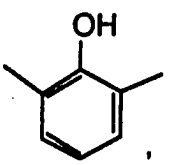

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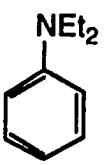
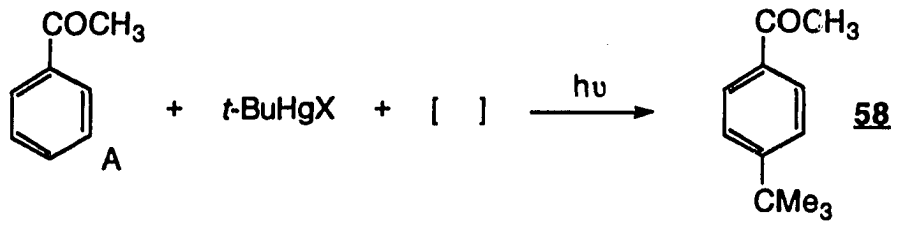


; recovered in all condition.

Table XXXIII. Photostimulated reactions of acetophenone with *t*-BuHgX in Me_2SO[a]

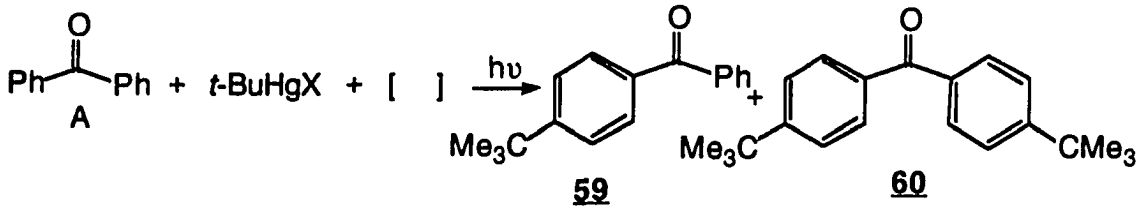


X	molar equivalents	time (h)	% yield[b]	
	t-BuHgX:KI:$K_2S_2O_8$:Dabco		A	**58**
Cl	4 : 0 : 0 : 0	47	85	5
Cl	4 : 4: 0 : 0	30	69	tr
I	4 : 4: 0 : 0	27	82	3
Cl	4 : 4: 2 : 0	22	78	2
Cl	4 : 0: 0 : 4	35	48	30
I	4 : 0: 0 : 4	47	61	30
I	6 : 0 : 0 : 6	44	57	32
I	4 : 4 : 0 : 4	27	65	22

[a]0.5 Mmol of acetophenone in 10 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]By GC with toluene as an internal standard.

Table XXXIV. Photostimulated reactions of benzophenone with *t*-BuHgX in Me_2SO[a]

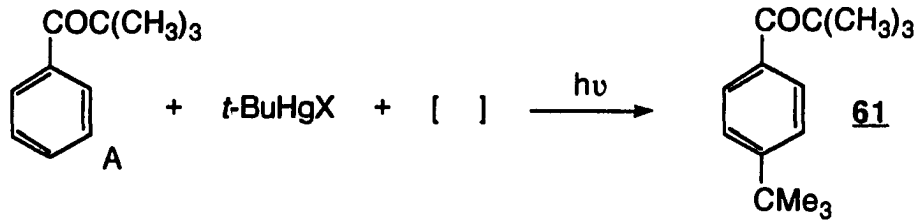


X	molar equivalents	time (h)		% yield[b]	
	t-BuHgX:KI:$K_2S_2O_8$:Dabco		A	59	60
Cl	6 : 0 : 0 : 0	31	41	9	-
I	6 : 0: 0 : 0	31	52	3	-
Cl	6 : 6: 0 : 0	31	36	32	5
Cl	6 : 0: 0 : 6	33	35	50	13
I	6 : 0: 0 : 6	33	17	46	20
Cl	6 : 6 : 0 : 6	33	30	34	8

[a]0.5 Mmol of benzophenone in 10 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]By GC with toluene as an internal standard.

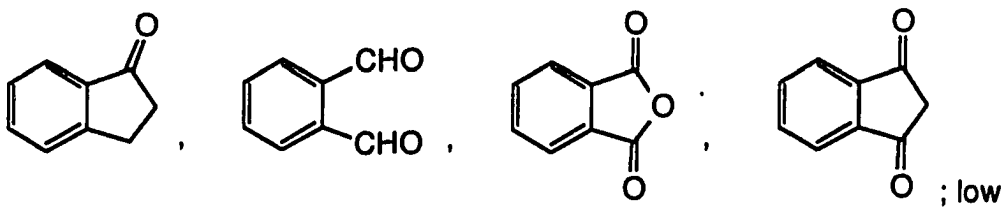
Table XXXV. Photostimulated reactions of *tert*-butyl phenyl ketone with *t*-BuHgX in Me_2SO[a]



X	molar equivalents	time (h)	% yield[b]	
	t-BuHgX:KI:Dabco		A	61
Cl	6 : 0 : 4	24	47	3
I	6 : 0: 6	53	47	19
Cl	6 : 6: 4	35	66	12
I	6 : 6 : 6	43	56	14

[a]0.5 Mmol of *tert*-butyl phenyl ketone in 10 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]By GC with toluene as an internal standard.



; low regioselectivity with low yields of alkylation products.

In the case of the photostimulated reaction of nitrobenzene with *t*-Bu•, aromatic substitution is not observed. Instead, any combination of *t*-BuHgX, KI, $K_2S_2O_8$, and a base deoxygenate nitrobenzene to yield products mainly derived from the resulting nitroso compounds (Scheme 23).

Scheme 23

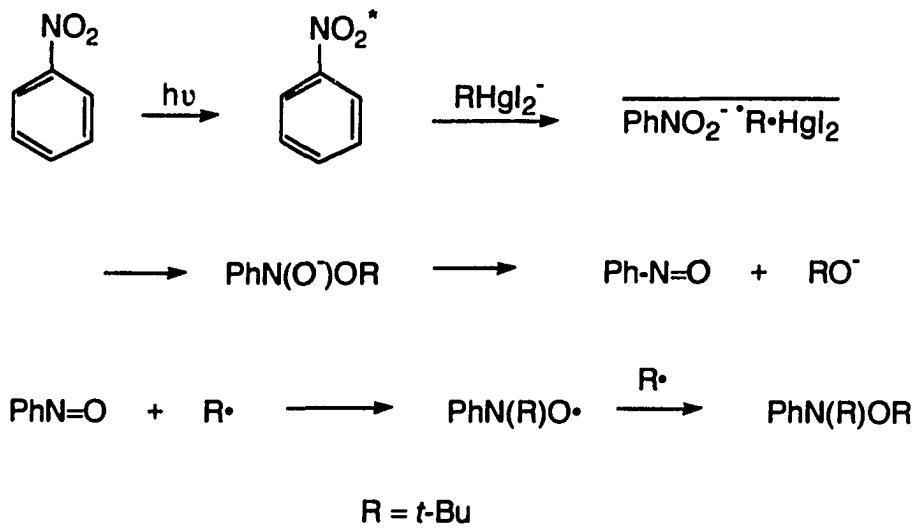
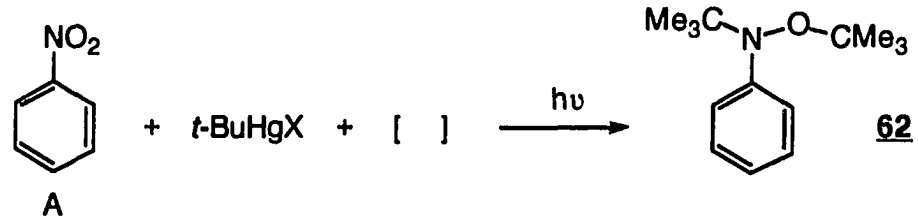


Table XXXVI. Photostimulated reactions of nitrobenzene with *t*-BuHgX in Me_2SO[a]



X	molar equivalents	time (h)	% yield[b]	
	t-BuHgX:KI:$K_2S_2O_8$:base		A	62
Cl	4 : 0 : 0 : Dabco (4)	24	66	2
Cl	4 : 4: 0 : Dabco (4)	24	32	4[c]
Cl	4 : 4: 2 : 0	30	0	23[c]
Cl	4 : 4: 2 : Dabco (4)	30	tr	23[c]
I	6 : 0 : 0 : KOH (4)	22[d]	27	36[c]
I	6 : 0 : 0 : KOH (4)	22[d]	0	53[c]

[a]0.5 Mmol of nitrobenzene in 10 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]By GC with toluene as an internal standard.

[c]2 - 8% of two by-products formed.

[d]8 Ml of benzene and 2 ml of water with 2 drops of Aliquat 336 were used as a solvent.

2. Cyclization reactions via free radical chain reactions

Intramolecular radical cyclization could occur if the adduct radical is in a proper position for the cyclization. Thus, 1-phenyl-4-penten-1-one cyclizes under many reaction conditions (Table XXXVII). Addition of Dabco increases the yield whereas addition of I^- seems to retard the reaction. Addition of Dabco seems to promote the chain reaction by proton removal from the cyclized educt radical (reaction 40 in Scheme 24). This process is more important than electron transfer from the educt radical to $RHgI_2^-$ (reaction 41 in Scheme 24).

Scheme 24

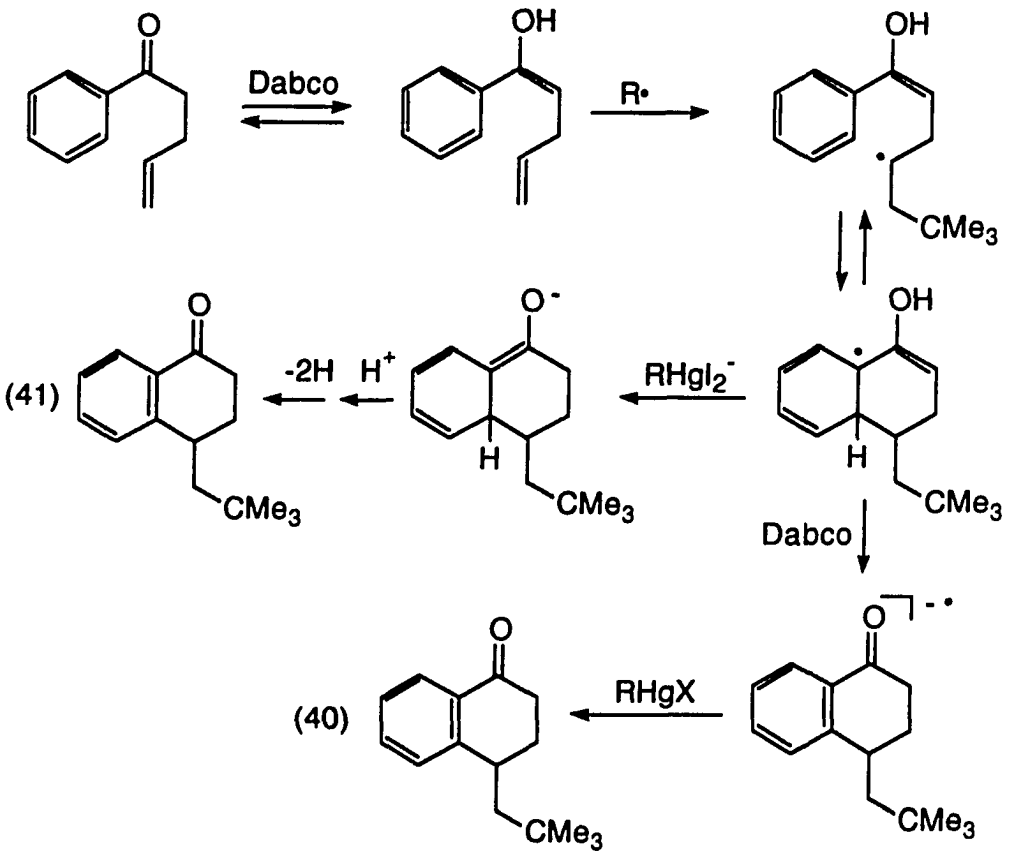
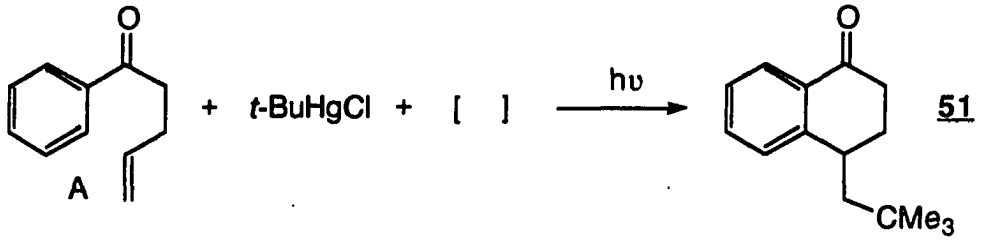


Table XXXVII. Photostimulated reactions of 1-phenyl-4-penten-1-one with *t*-BuHgCl in Me_2SO[a]



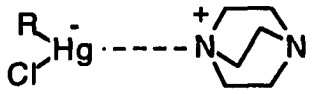
51

molar equivalents	time (h)	% yield[b]	
t-BuHgCl:KI:$K_2S_2O_8$:Dabco		A	51
4 : 0 : 0 : 0	26	40	23
6 : 0: 0 : 4	24	14	42
4 : 8 : 0 : 0	26	68	8
4 : 4: 0 : 4	22	42	30
4 : 0: 2 : 0	24	74	8
4 : 4 : 2 : 0	24	27	43
4 : 4 : 2 : 4	24	30	30

[a]0.5 Mmol of substrate in 25 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

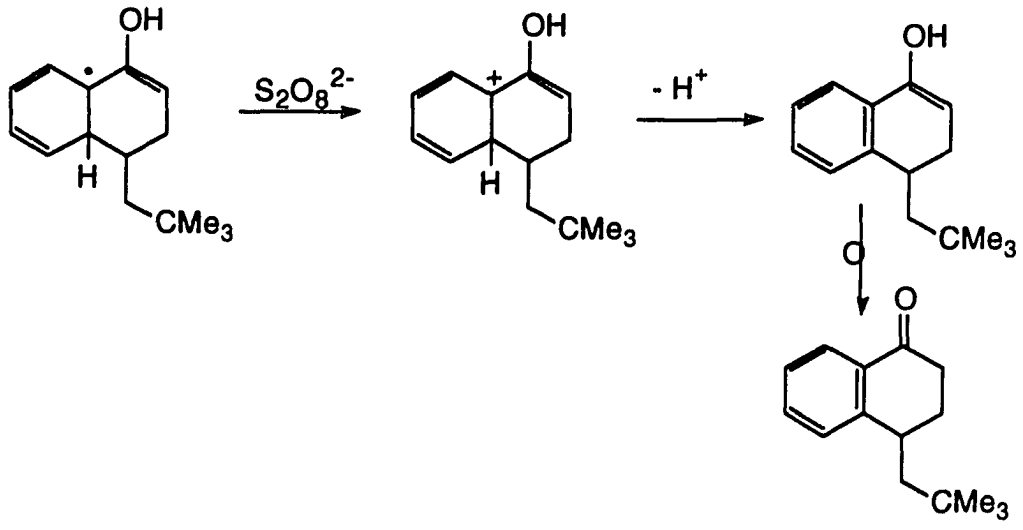
[b]By GC with toluene as an internal standard.

Presumably Dabco controls the rate of *t*-Bu• formation. With KI, formation of *t*-Bu• may be too fast for the cyclization reaction to occur efficiently. Dabco possibly makes a complex with RHgCl which produce the radical faster than RHgCl itself but slower than in the RHgCl/KI system.



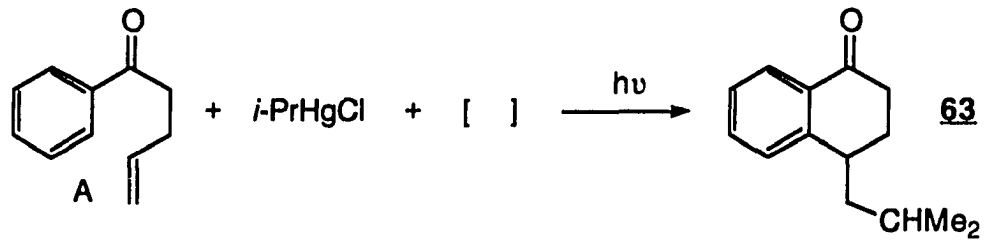
t-BuHgCl/KI/$K_2S_2O_8$ works fairly well for the cyclization reaction, possibly because because $S_2O_8^{2-}$ oxidizes the adduct radical to produce the cyclized product via Scheme 25.

Scheme 25



Isopropylmercury chloride reactions shows similar results even though the yields are usually lower than in the *t*-BuHgCl reactions (Table XXXVIII). With *i*-

Table XXXVIII. Photostimulated reactions of 1-phenyl-4-penten-1-one with *i*-PrHgCl in Me_2SO[a]



63

molar equivalents	time (h)	% yield[b]	
i-PrHgCl:KI:$K_2S_2O_8$:Dabco		A	63
6 : 0 : 0 : 0	24	60	9
4 : 0: 0 : 4	27	30	37
6 : 4 : 0 : 0	24	27	15
6 : 4: 0 : 4	26	12	23
4 : 4 : 2 : 0	24	32	38
6 : 4 : 2 : 4	26	25	19

[a]0.5 Mmol of substrate in 25 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]By GC with toluene as an internal standard.

PrHgCl (4 equiv)/Dabco (4 equiv), the reaction produces cyclized product **63** (37%) with the starting substrate remained. With *i*-PrHgCl (4 equiv)/KI (4 equiv)/$K_2S_2O_8$ (2 equiv), the reaction produced 38% of **63** presumably via Scheme 25.

Radical initiated cyclizations of *N*-but-3-enyl-*N*-methylaminobenzene showed fairly good results (Table XXXIX). Yields are improved by using *t*-BuHgI/Dabco (55%) instead of *t*-BuHgCl/Dabco (43%). With both *t*-BuHgI and *t*-BuHgCl, the presence of Dabco increases the yield. The reaction apparently follows Scheme 26.

Scheme 26

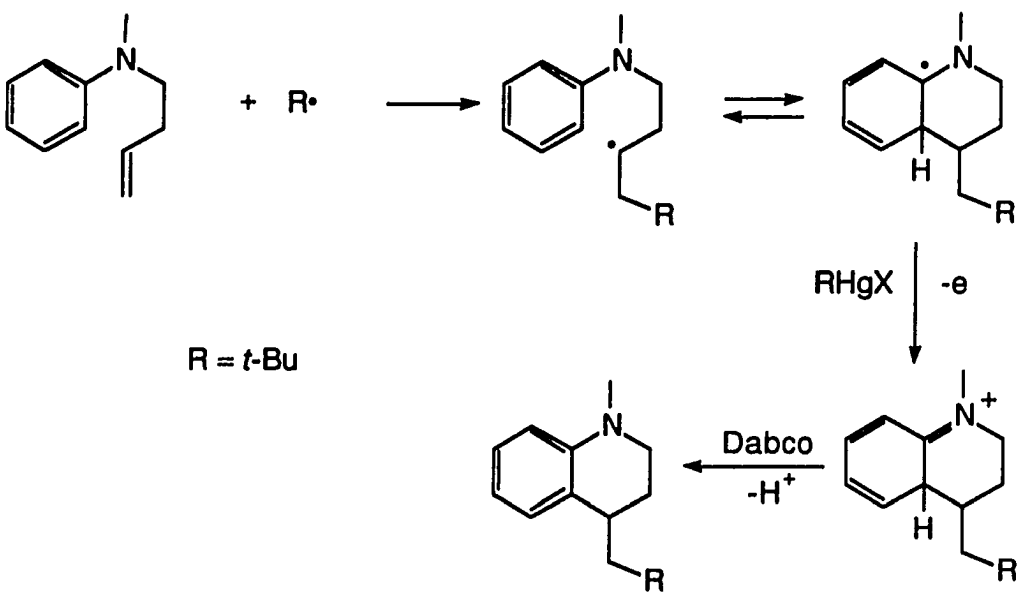
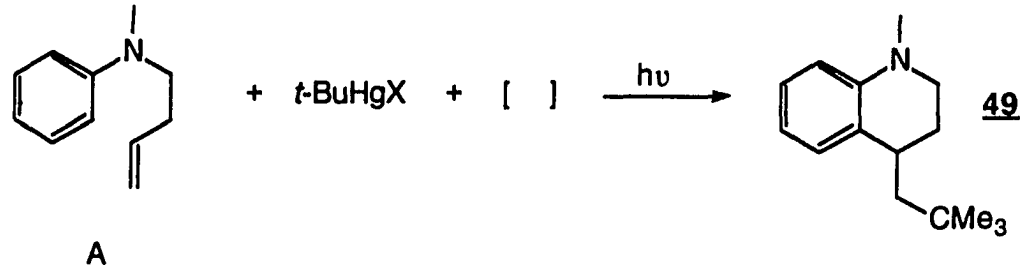


Table XXXIX. Photostimulated reactions of *N*-but-3-enyl-*N*-methylaminobenzene with *t*-BuHgX in Me_2SO[a]



A

49

X	molar equivalents	time (h)	% yield[b]	
	t-BuHgX:KI:$K_2S_2O_8$:Dabco		A	**49**
Cl	6 : 0 : 0 : 0	48	32	22
Cl	6 : 0 : 0 : 6	48	15	43
I	6 : 0 : 0 : 0	36	6	43
I	6 : 0 : 0 : 6	48	8	55
Cl	6 : 6 : 0 :0	42	29	26
Cl	6 : 6 : 0 : 6	26	39	35
Cl	6 : 6 : 2 : 0	42	4	25
I	6 : 6 : 0 : 0	36	4	46
I	6 : 6 : 0 : 6	26	9	17

[a]0.5 Mmol of *N*-but-3-enyl-*N*-methylaminobenzene in 10 ml of Me_2SO irradiated with a 275-W GE sunlamp at ~40 °C.

[b]By GC with toluene as an internal standard.

Radical initiated cyclization of *N*-allyl-*N*-methylaminobenzene which could form a 5-membered ring was not successful; the reaction produces *N*-methyl-aniline as a major product via cleavage of N-C bond accompanied by cyclized and di-*tert*-butylated products.

C. Conclusion

Reaction of aromatic carbonyl compounds, such as benzaldehyde, with *tert*-butyl radical yields exclusively the product of *para*-alkylation via a radical chain reaction in the presence of Dabco. Dabco increases the yield by abstracting the proton from the educt radical to form the radical anion.

Isopropyl radical produces a mixture of the ortho, meta, para alkylation products. Radical cyclization is observed by same technique. 1-Phenyl-4-penten-1-one and *N*-but-3-enyl-*N*-methylaminobenzene are cyclized to produce 6-membered ring by the radical attack of R• upon the terminal alkene position followed by cyclization to the aromatic ring.

D. Experimental Section

1. General consideration

Analytical gas chromatography (GC) was performed on a Varian 3700 gas chromatograph equipped with a Hewlett-Packard 3390A integrator. ^1H and spectra were recorded on a 300 MHz Nicolet NT300 spectrometer. Chemical shifts were reported in ppm from tetramethylsilane (TMS). 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 Digilab FTS-7 FT spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected.

Most products were isolated by flash column chromatography on silica gel (Kiesel gel, 230-400 mesh ATSM, purchased from EM Regents Co.) with eluents of mixed solvents. GC yields were determined by using an internal standard (toluene) and were corrected with predetermined response factors.

tert-Butyl halides were prepared as previously described in Chapter I. Solvents were purchased and dried as mentioned before. Chemical reagents were purchased mostly from Aldrich and the reagents were used without further purification in most cases.

2. Preparation of 1-phenyl-4-penten-1-one[90]

KH was transfered to the 250 ml flask and washed with THF three times and flushed with nitrogen and weighed (~0.05 mol). After introduction of 100 ml of THF, acetophenone (0.047 mol) was added by using a syringe and 0.059 mol of Et_3B (1 M solution) was dropped into the solution at room temperature. Allyl bromide (0.071 mol) was dropped into the solution and stirred for 3 hours at room temperature. The reaction was quenched with $NaOH/H_2O_2$ solution and washed twice with $NaHCO_3$ solution and once with brine solution. Organic layer was dried over $MgSO_4$, concentrated, and passed through a silica gel column. The product was obtained in 80% yield; ^1H NMR ($CDCl_3$), δ 2.43 -2.48 (m, 2H), 3.02 - 3.07 (m, 2H), 5.00 - 5.08 (m, 2H), 5.82 - 6.00 (m, 2H), 7.40 - 7.60 (m, 3H), 7.90 - 8.20 (broad d, 2H).

3. Preparation of *N*-but-3-enyl-*N*-methylaminobenzene[91]

A mixture of *N*-methylaniline (0.019 mol), 4-bromo-but-1-ene, and sodium carbonate (0.011 mol) in EtOH (8 ml)/ H_2O (2 ml) was heated under reflux with stirring for 15 hours under nitrogen. The solvent was evaporated after the reaction was completed and 10% aqueous NaOH solution was added. The mixture was extracted three times with dichloromethane and the combined extract was washed with water twice and dried over $MgSO_4$. After concentration, the product was distilled to yield 52% of the desired product; ^1H NMR ($CDCl_3$), δ 2.27 -2.36 (m, 2H), 2.93 (s, 3H), 3.38 (broad t, 2H J = 7.5 Hz), 5.00 - 5.14 (m, 2H), 5.74 - 5.90 (m, 1H), 6.65 - 6.72 (m, 3H), 7.19 - 7.26 (m, 2H).

4. General procedure for photostimulated alkylations of aromatic compounds and cyclization reactions

The substrate (0.5 mmol), RHgX (2.0 - 3.0 mmol), and coreactants were dissolved in 10 ml of deoxygenated Me_2SO in a pyrex tube equipped with a rubber septum. The mixture was irradiated under nitrogen by a 275-W GE sun lamp ca. 25 cm from the reaction tube. The reaction was quenched with aqueous sodium thiosulfate and extracted with ether. The ether extract was washed with aqueous sodium thiosulfate, dried over $MgSO_4$, and the solvent evaporated. The GC yield was determined with an internal standard (toluene) and if necessary, the products were isolated by flash column chromatography (silica gel) with ethyl acetate (2%) - hexane (98%).

a. 4-(2,2-Dimethylpropyl)-1-methyl-1,2,3,4-tetrahydroquinoline (49)

After separation, 49 was obtained in 87% purity; 1H NMR ($CDCl_3$) δ 1.00 (s, 9H), 1.50 (d, 2H, J = 5.1 Hz), 1.75 - 1.85 (m, 1H), 1.94 - 2.06 (m, 1H), 2.81 - 2.89 (m,

1H), 2.88 (s, 3H, N-CH_3), 3.07 - 3.15 (m, 1H), 3.25 (dt (overlapping ddd), 1H, *J* = 3.6,11.4 Hz), 6.57 - 6.66 (m, 2H), 6.98 - 7.09 (m, 2H); GCMS m/z (relative intensity) 217 (M^+, 22), 202 (0.3), 160 (2), 146 (100), 131 (9), 57 (2); HRMS m/z cald for $C_{15}H_{23}N$ 217.1831, found 217.1831.

b. 3,4-Dihydro-4-(2,2-dimethylpropyl)-1(2*H*)-naphthalenone (51) The compound was an oily liquid; ^1H NMR ($CDCl_3$) δ 1.04 (s, 9H), 1.50 (dd, 1H, *J* = 2.1, 14.4 Hz), 1.75 (dd, 1H, *J* = 7.8, 14.4 Hz), 2.11 (dq, 1H, *J* = 18.0, 4.5 Hz), 2.20 - 2.33 (m, 1H), 2.57 (dt, 1H, *J* = 17.4, 4.8 Hz), 2.83 (ddd, 1H, *J* = 17.4, 12.3, 4.8 Hz), 3.02 - 3.12 (m, 1H), 7.24 - 7.30 (bd t, 2H), 7.48 (t, 1H, *J* = 7.2 Hz), 7.99 (d, 1H, *J* = 7.2 Hz); GCMS m/z (relative intensity) 216 (M^+, 42), 201 (1), 160 (5), 145 (100), 131 (21), 117 (30), 103 (7), 91 (13), 57 (25); HRMS m/z cald for $C_{15}H_{20}O$ 216.1514, found 216.1517; FTIR ($CDCl_3$) 3063 (w), 2852 (s), 2865 (m), 1686 (vs) cm^{-1}.

c. 4-(1,1-Dimethylethyl)benzaldehyde (54)[92] The compound was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 1.36 (s, 9H), 7.55 (d, 2H, *J* = 8.4 Hz), 7.82 (broad d, 2H, *J* = 8.4 Hz), 9.98 (s, 1H); GCMS m/z (relative intensity) 162 (M^+, 40), 147 (100), 119 (32), 91 (50), 77 (14), 41 (40); HRMS m/z cald for $C_{11}H_{14}O$ 162.1045, found 162.1049; FTIR($CDCl_3$) 2962 (m), 2907 (m), 2867 (m), 1699 (s), 1674 (w) cm^{-1}.

d. 1-[4-(1,1-Dimethylethyl)phenyl]ethanone (58)[93] The compound was obtained as a liquid; ^1H NMR ($CDCl_3$) δ 1.34 (s, 9H), 2.59 (s, 3H), 7.48 (d, 2H, *J* = 8.1 Hz), 7.90 (d, 2H, *J* = 8.1 Hz); GCMS m/z (relative intensity) 176 (M^+, 28), 161 (89), 146 (6), 133 (13), 115 (9), 105 (8), 91 (11), 77 (8), 43 (100); HRMS m/z cald for $C_{12}H_{16}O$ 176.1201, found 176.1205; FTIR ($CDCl_3$) 2941 (m), 2870 (w), 1684 (s), 1607 (m) cm^{-1}.

e. 4-(1,1-Dimethylethyl)benzophenone (59)[94] The compound was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 9H), 7.42 - 7.61 (m, 5H), 7.74 - 7.82 (m, 4H); GCMS (relative intensity) 238 (M^+, 35), 223 (100), 161 (17), 105 (55), 77 (49); HRMS m/z cald for $C_{17}H_{18}O$ 238.1358, found 238.1354; FTIR (neat) 3058 (w), 2961 (m), 1658 (vs), 1603 (s) cm^{-1}.

f. 4,4'-Di-(1,1-dimethylethyl)benzophenone (60)[95] The compound had mp 105 - 109 °C; ^{1}H NMR ($CDCl_3$) δ 1.37 (s,18H), 7.49 (d, 4H, *J* =8.4 Hz), 7.76 (d, 4H, *J* = 8.4Hz); GCMS m/z 294 (M^+, 23), 279 (100), 161 (32), 104 (22); HRMS m/z cald for $C_{21}H_{26}O$ 294.1984, found 294.1976; FTIR ($CDCl_3$) 2964 (s), 1652 (s), 1604 (s) cm^{-1}.

g. 2,2-Dimethyl-1-[4-(1,1-dimethylethyl)phenyl]-1-propanone (61)[96] The compound was a liquid; ^{1}H NMR ($CDCl_3$) δ 1.33(s, 9H), 1.36 (s, 9H), 7.41 (d, 2H, *J* = 8.1 Hz), 7.71 (d, 2H, *J* = 8.1 Hz); GCMS m/z (relative intensity) 218 (M^+, 1), 161 (100), 146 (7), 118 (9), 91 (9), 57 (9); HRMS m/z cald for $C_{11}H_{13}O$ (M - C_4H_9) 161.0967, found 161.0965; FTIR ($CDCl_3$) 2958 (s), 2925 (m), 2866 (s), 1670 (s) cm^{-1}.

h. *N*-(1,1-dimethylethoxy)-*N*-(1,1-dimethylethyl)aniline (62) The compound was a liquid; ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 9H), 1.07 (s, 9H), 7.01 - 7.08 (m, 2H), 7.16 - 7.26 (m, 3H); ^{13}C NMR ($CDCl_3$) 26.827, 28.156, 59.371, 77.980, 124.327, 125.973, 127.081, 151.125; GCMS m/z (relative intensity) 221 (M^+, 1), 165 (18), 109 (100), 57 (48): CI (NH_3) 222 (MH^+); HRMS m/z cald for $C_{14}H_{23}NO$ 221.1780, found 221.1781.

i. 3,4-Dihydro-4-(2-methylpropyl)-1(2*H*)-naphthalenone (63) The compound was an oily liquid; ^{1}H NMR ($CDCl_3$) δ 1.43 (t (overlapping doublets), 6H), 1.43 -1.81 (m, 3H), 1.97 - 2.08 (m, 1H), 2.16 - 2.31 (m, 1H), 2.52 - 2.63 (m,

1H), 2.69 - 2.83 (m, 1H), 2.93 - 3.06 (m, 1H), 7.24 - 7.33 (m, 2H), 7.48 (dd, 1H, J = 7.8, 1.2 Hz), 8.01 (d, 1H, J = 7.8 Hz); GCMS m/z (relative intensity) 202 (M^+, 29), 145 (100), 131 (19), 117 (34), 104 (27), 91 (12), 77 (9); HRMS m/z cald for $C_{14}H_{18}O$ 202.1358, found 202.1362; FTIR (neat) 2954 (m), 2924 (m), 2866 (w), 1684 (s) cm^{-1}.

IV. SUMMARY

Photostimulated chain reactions of alkylmercury halides with α,β-unsaturated carbonyls or 1.4-enediones yields the reductive alkylation product in the presence of I^- or $I^-/S_2O_8^{2-}$. In the presence of a base such as Dabco the intermediate enolyl radical forming from by free radical addition to 1,4-enediones can be deprotonated to a radical anion which yields the oxidative alkylation product upon electron transfer to the alkylmercury halide. The competition between proton loss to Dabco from the enolyl radical and electron transfer from $RHgI_2^-$ to the enolyl radical increasingly favors the electron transfer process as R of the alkylmercurial is changed from *n*-Bu to *i*-Pr to *t*-Bu as demonstrated by reactions of both acyclic 1,4-enediones and naphthoquinone. The effectiveness of alkylmercurials in the enolyl radical to enolate anion conversion shows in the order of *t*-BuHgI/I^- ≥ *t*-BuHgCl/I^- > *t*-BuHgI > *t*-BuHgCl. The measured initial kinetic chain length for the reaction of *t*-BuHgI with *N*-methylmaleimide is ~200. Relative reactivities of various compounds towards *tert*-butyl radical attack have been determined. In the presence of PTSA or TMSI the reactivity of imines towards *tert*-butyl radical addition is enhanced by 3 - 410 times depending upon the substrate. Substitution reactions of aromatic compounds which have an electron-withdrawing group produce exclusively the product of *para*-alkylation via a radical chain reaction with *tert*-butyl radical by use of the oxidative alkylation technique. Radical cyclization occurs with 1-phenyl-4-penten-1-one and *N*-bet-3-enyl-*N*-methylaminobenzene which is initiated by the radical addition of R• to the

terminal alkene position followed by cyclization, proton removal, and electron transfer to alkylmercury halide.

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Also, thanks go to the members of the Russell group for their friendship and assistance.

To my parents in Korea, who have given me their constant support and encourgement throughout my education, I give my most sincerest thanks. I am deeply grateful to my lovely son, Jae Hoon, and my wife, Kyu Hwa, who stood by me through the good and bad times.

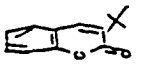
VII. APPENDIX

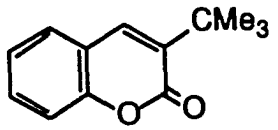
NMR SPECTRA OF NEW COMPOUNDS

The following ^1H NMR spectra of new compounds are provided to show adequate evidence to establish identity and purity. Exact positions of peaks, coupling constants, and proton integrations are available in experimental sections of the text.

BHK 226 1SU 02NOV88
H/DABCO. IN DMSO

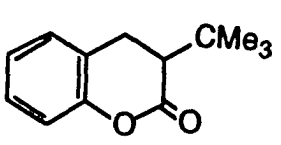
3-*tert*-Butylcoumarin





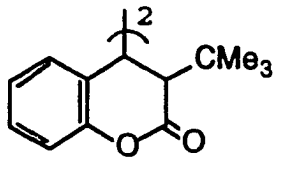
2

KB
SEP. SA-. **3-*tert*-Butyldihydrocoumarin**



3

KY . 646 ISU OBJAN90
SEP.



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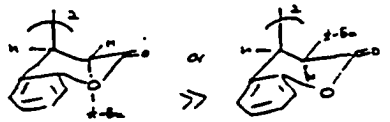
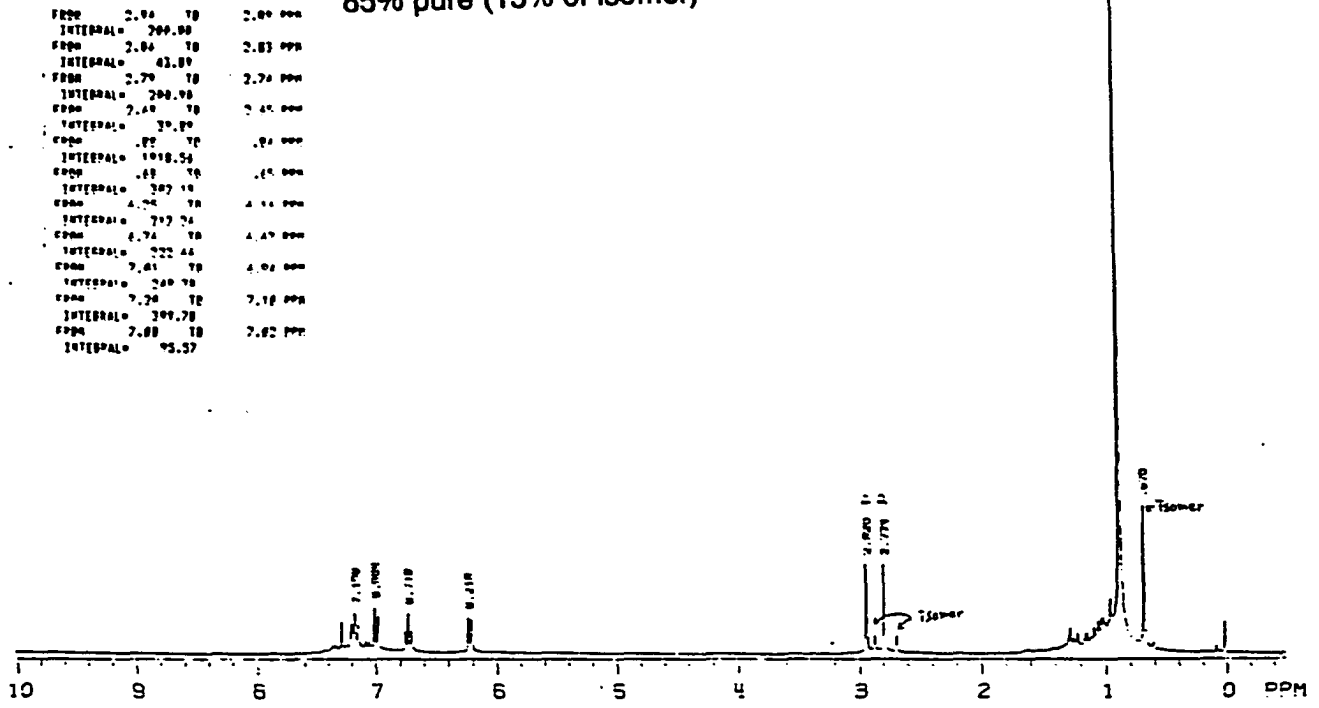
3,3'-Di-*tert*-butyl-4,4'-bidihydrocoumarin

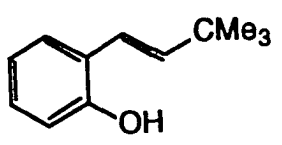


85% pure (15% of isomer)



BHK 234 ISU 03NOV88
234 PD

(*E*)-2-(3,3-Dimethyl-1-butenyl)-phenol



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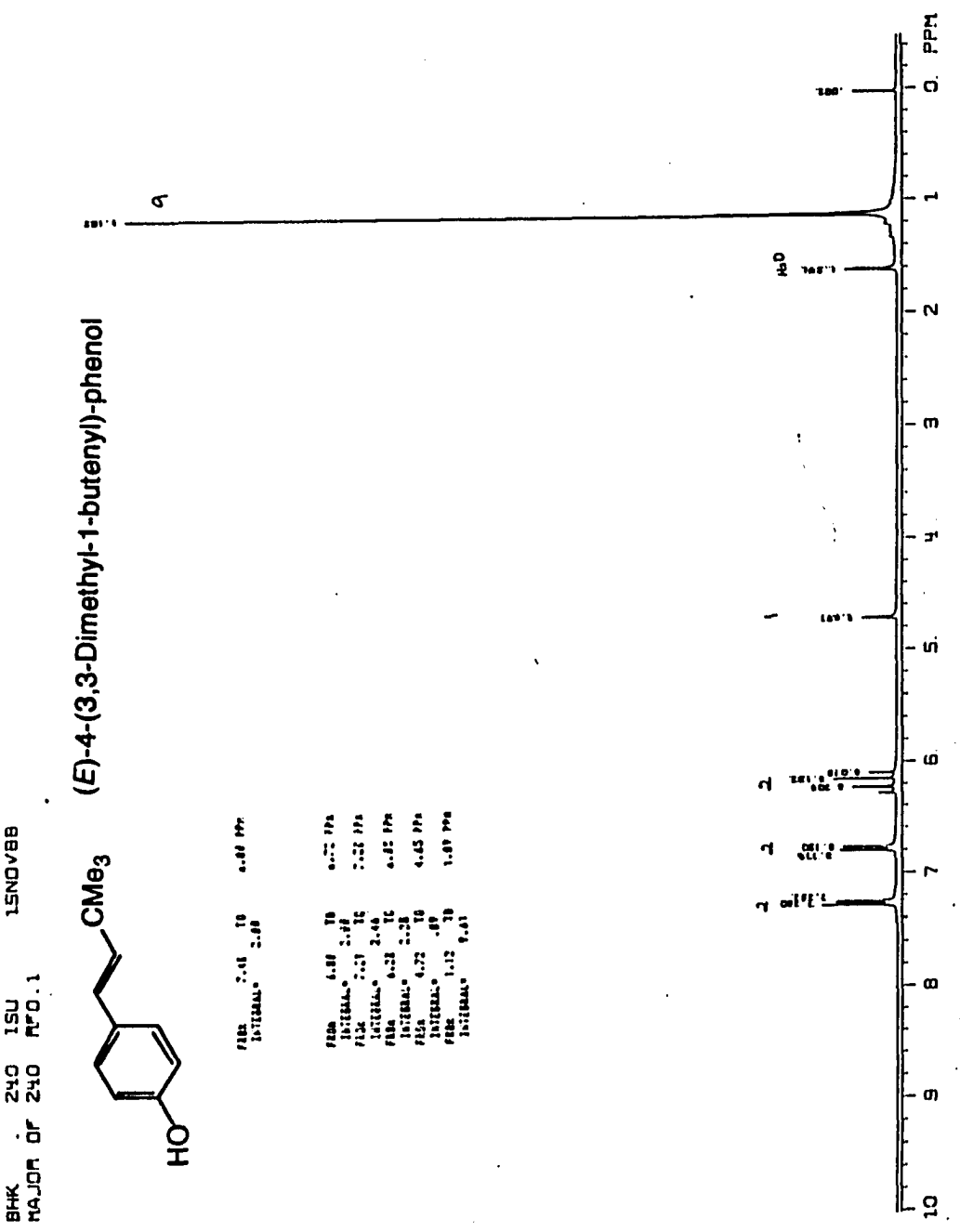
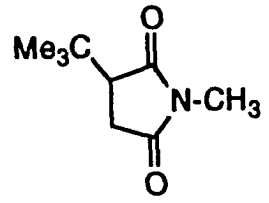

(E)-4-(3,3-Dimethyl-1-butenyl)-phenol
CMe3
HO
BHK 240 1SU 1SNOVBB
MAJOR OF 240 RFO.1
H2O
PPM

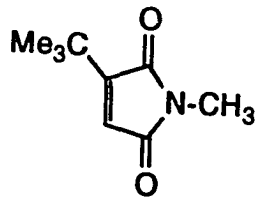
KRB . 525 F 2.SEP89
SEP.



9

3-(1,1-Dimethylethyl)-1-methyl-2,5-pyrrolydinedione

X2 . 53.1 ISU . . . 27SEP89
SEP. 5 1

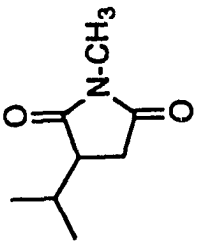


10

3-(1,1-Dimethylethyl)-1-methyl-1*H*-pyrrole-2,5-dione

FROM 6.25 TO 6.16 PPM
INTEGRAL= 1.00
FROM 2.99 TO 2.92 PPM
INTEGRAL= 2.91
FROM 1.33 TO 1.25 PPM
INTEGRAL= 9.03

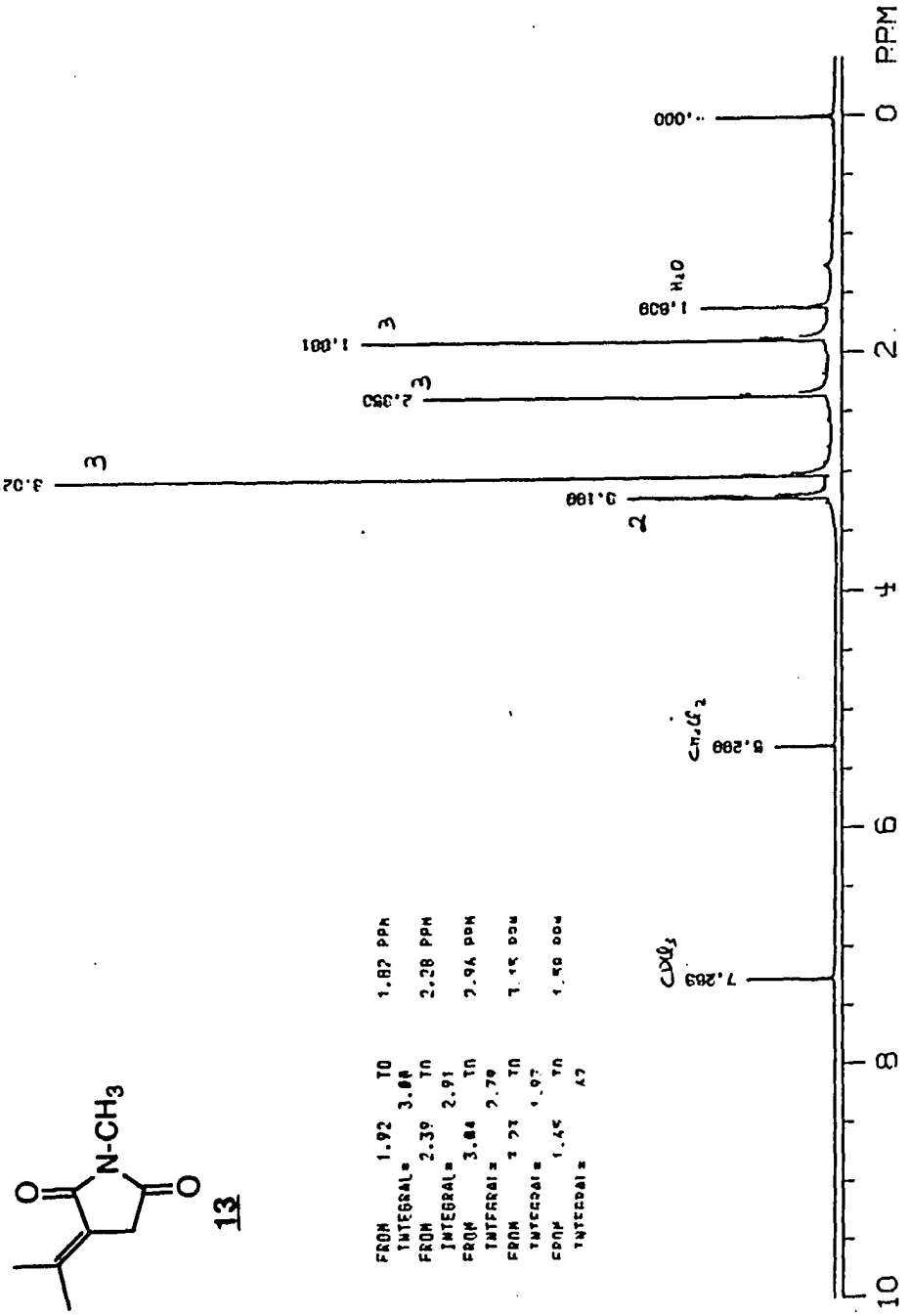
1-Methyl-3-(1-methylethyl)-2,5-pyrrolidinedione



11

FROM 1.02 TO .96 PPM
INTEGRAL- 300.00
FROM .89 TO .83 PPM
INTEGRAL- 299.55
FROM 2.80 TO 2.93 PPM
INTEGRAL- 283.31
FROM 2.53 TO 2.33 PPM
INTEGRAL- 184.74
FROM 2.39 TO 2.33 PPM
INTEGRAL- 98.77

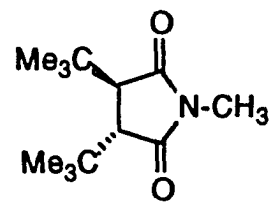
1-Methyl-3-(1-methylethylidene)-2,5-pyrrolidinedione



3,4-Bis(1-methylethyl)-1-methyl-1*H*-pyrrole-2,5-dione

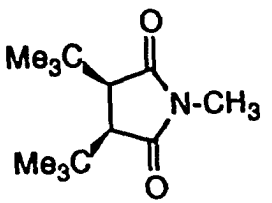
14

(*E*)-3,4-Bis(1,1-dimethylethyl)-1-methyl-2,5-pyrrolidinedione



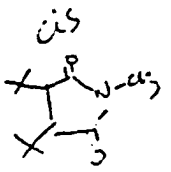
15a

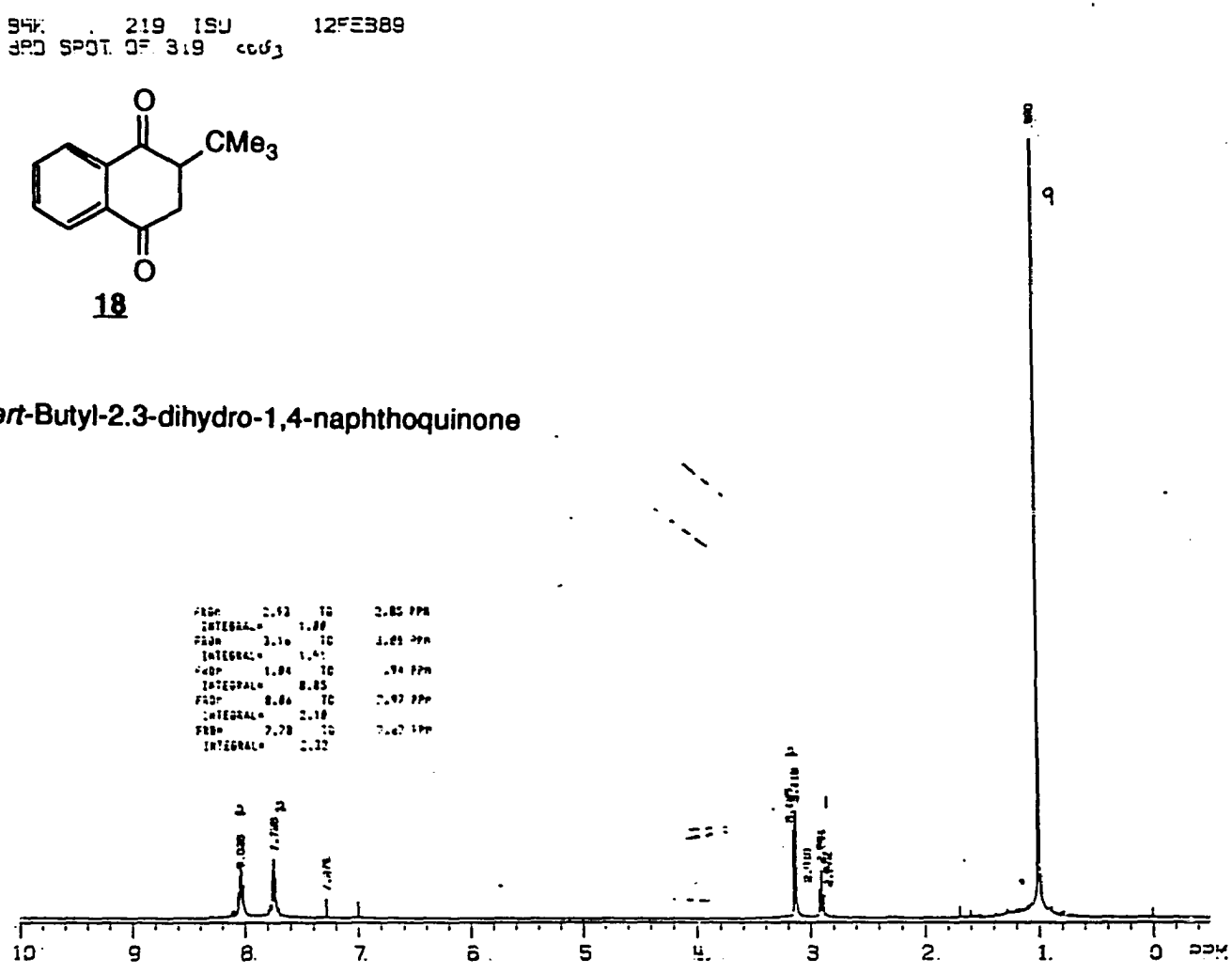
KC2. . .. 603. ISU 07.NOV89.
SEP. .



15b

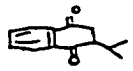
(Z)-3,4-Bis(1,1-dimethylethyl)-1-methyl-2,5-pyrrolidinedione



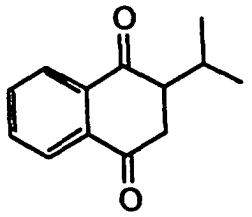


2-*tert*-Butyl-2.3-dihydro-1,4-naphthoquinone

KA2 . 473 15U 27JUL85
SEP.



KA2 · 473



21

FROM	2.34	TO	2.15 PPM
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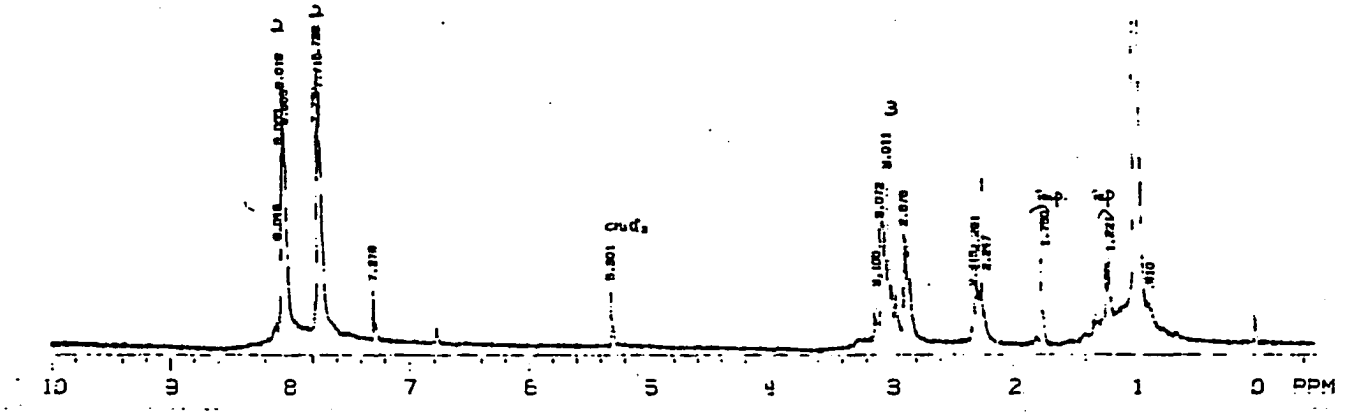
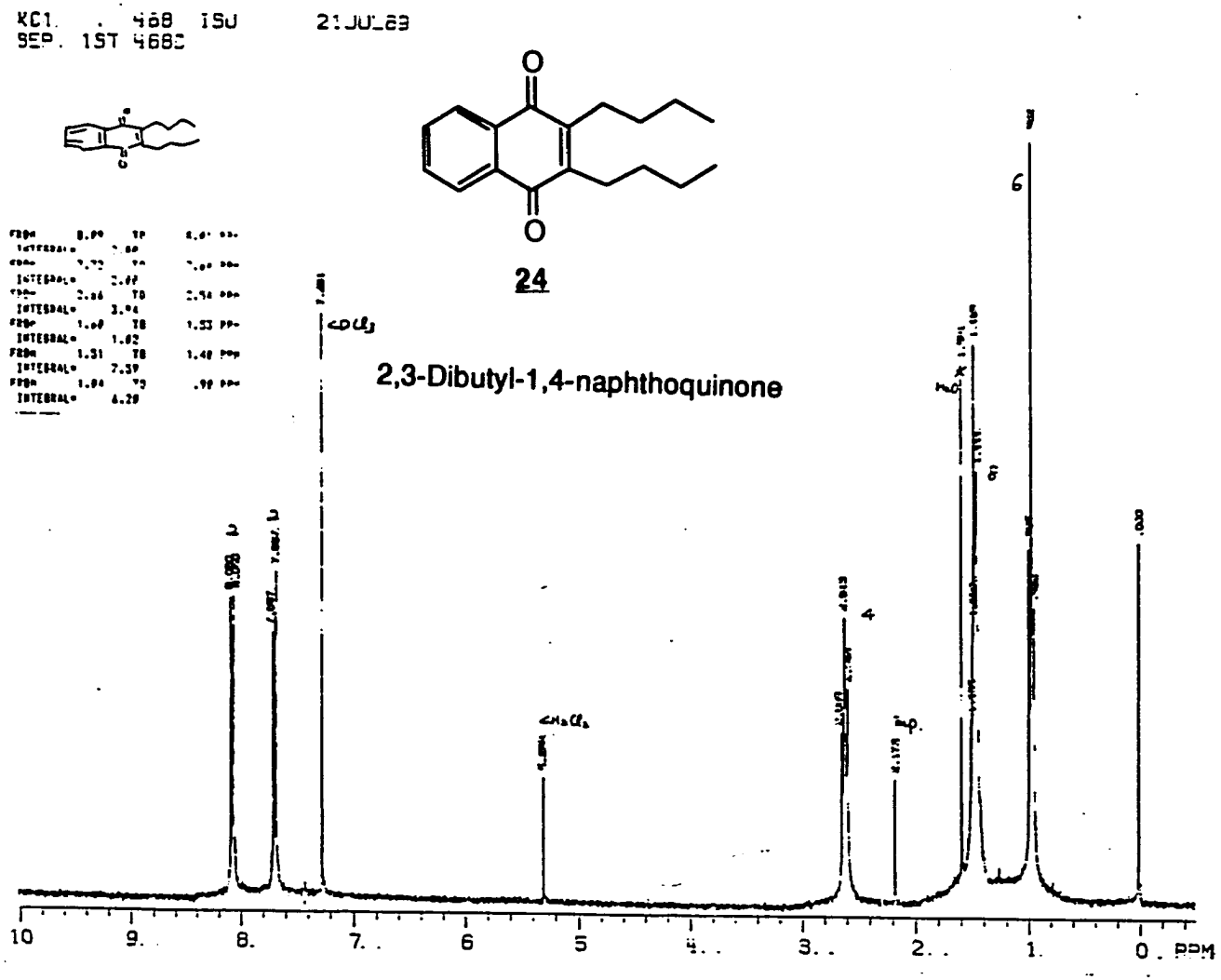
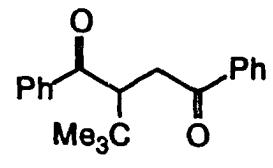
FROM	3.14	TO	2.92 PPM
INTEGRAL=	2.84		
FROM	2.92	TO	2.79 PPM
INTEGRAL=	1.03		
FROM	1.04	TO	.89 PPM
INTEGRAL=	6.27		
FROM	8.07	TO	7.93 PPM
INTEGRAL=	2.13		
FROM	7.78	TO	7.65 PPM
INTEGRAL=	2.32		

2,3-Dihydro-2-isopropyl-1,4-naphthoquinone




24
2,3-Dibutyl-1,4-naphthoquinone
10
9.
8.
7.
6
5
4.
3.
2.
1.
0. PPM



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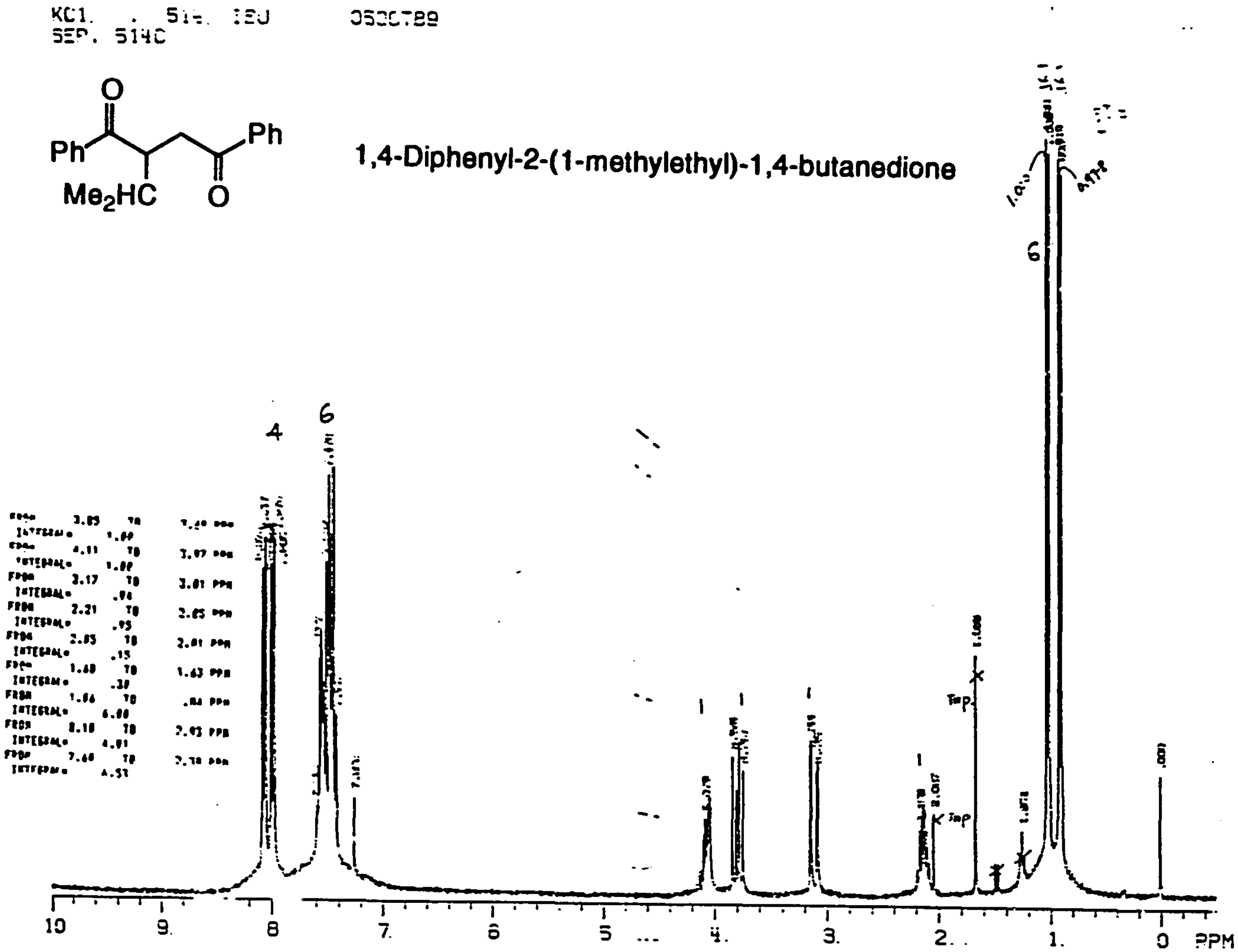
0520789
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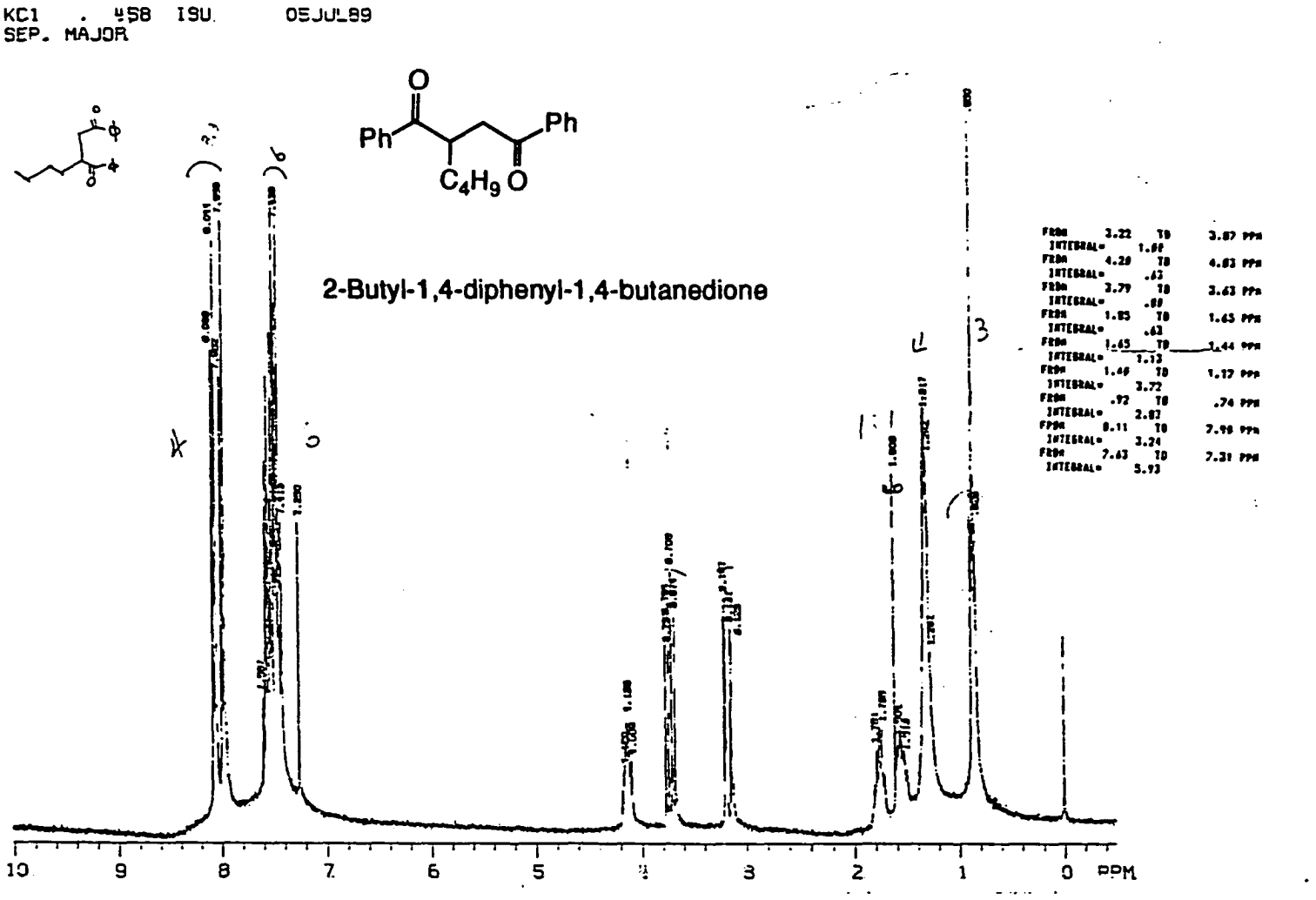
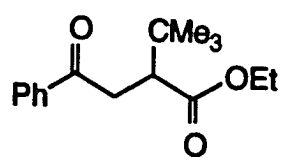
Me2HC
1,4-Diphenyl-2-(1-methylethyl)-1,4-butanedione
10
9.
8
7.
6
5
4.
3.
2.
1.
0
PPM


KC1 . 458 ISU 05JUL89
SEP. MAJOR
Ph
Ph
C_4H_9 O
2-Butyl-1,4-diphenyl-1,4-butanedione
10
9
8
7
6
5
4
3
2
1
0
PPM

K1 . 510 ISU 29AUG89
SEP. 1ST



Ethyl 2-(1,1-dimethylethyl)-4-oxo-benzenebutanoate

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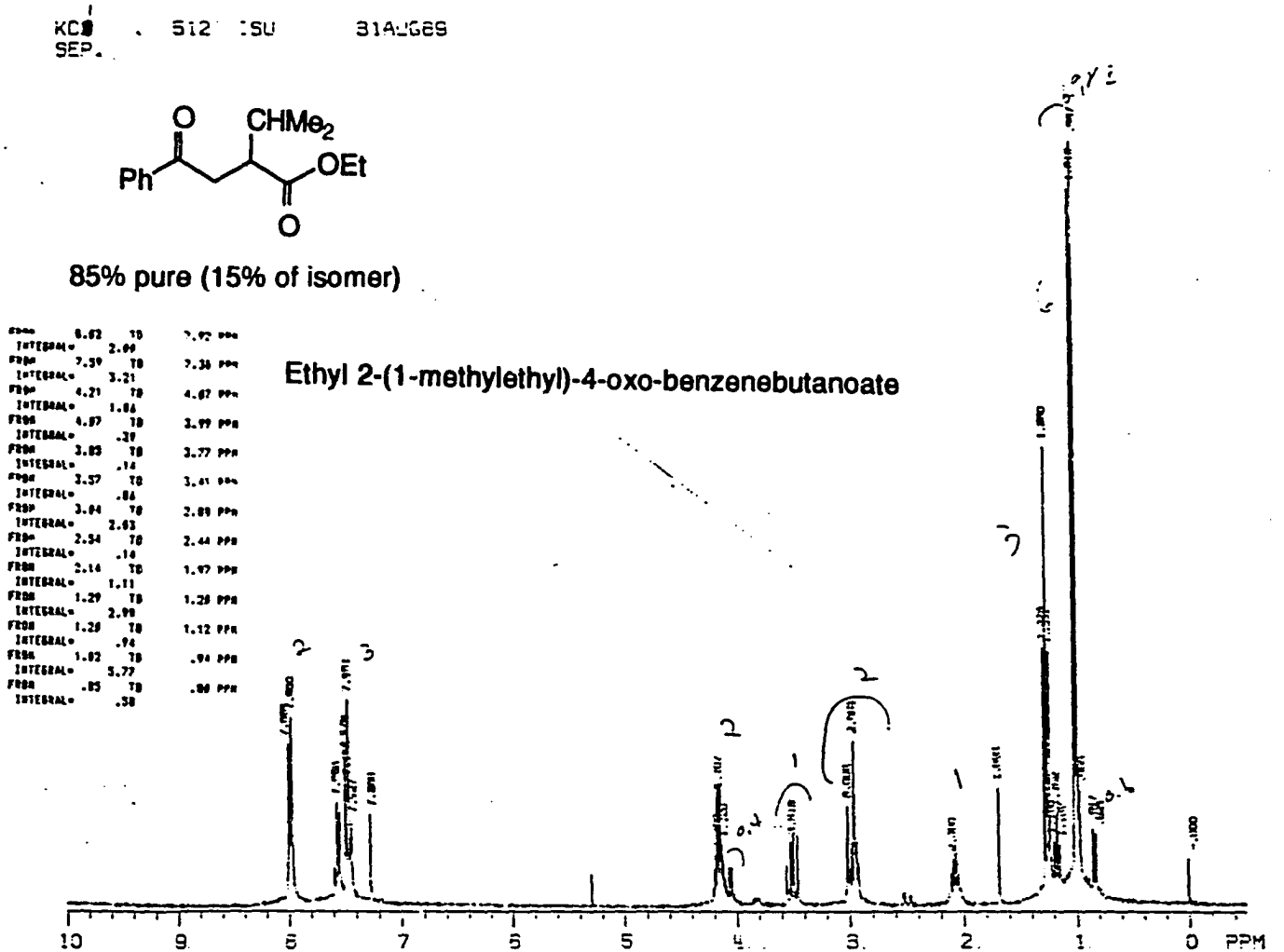
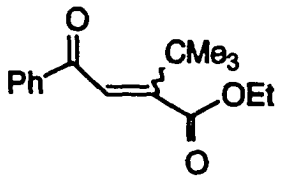
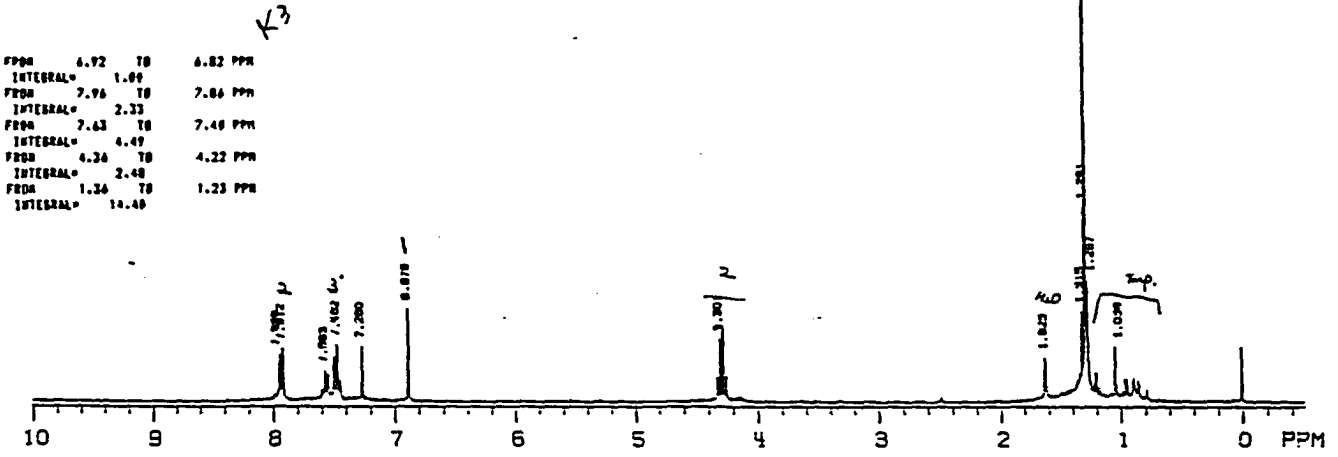
INTEGRAL=	2.00		
FP00	7.39	TO	7.39 PPM
INTEGRAL=	3.43		
FP00	4.21	TO	4.07 PPM
INTEGRAL=	1.99		
FP00	3.60	TO	3.46 PPM
INTEGRAL=	1.35		
FP00	3.12	TO	3.01 PPM
INTEGRAL=	1.00		
FP00	2.87	TO	2.77 PPM
INTEGRAL=	.97		
FP00	1.30	TO	1.23 PPM
INTEGRAL=	3.27		
FP00	1.05	TO	.98 PPM
INTEGRAL=	8.33		


KC
SEP.
512
CHMe2
OEt
Ph
O
O
85% pure (15% of isomer)
Ethyl 2-(1-methylethyl)-4-oxo-benzenebutanoate
10
9
8
7
6
5
4
3
2
1
0
PPM

K3 . 511 ISU 19SEP89
SEP. 511



Ethyl 2-(1,1-dimethylethyl)-4-oxo-4-phenylbutenoate



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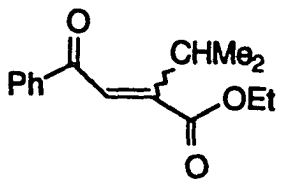

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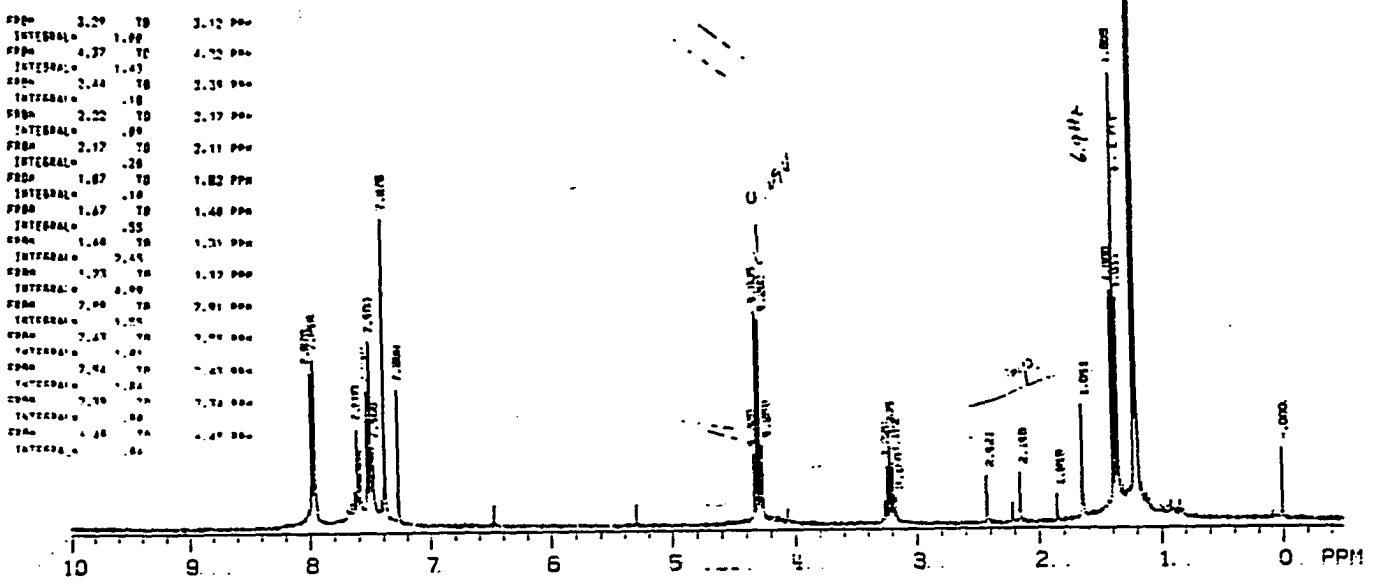
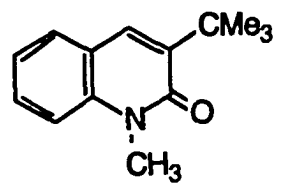


K . 115 1V 07JAN9
SEP.

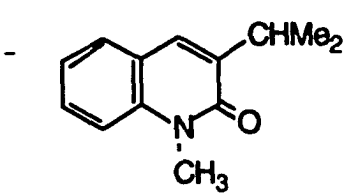


27

3-(1,1-Dimethylethyl)-1-methyl-2(1*H*)-quinolinone

FROM	7.56 TO	7.46 PPM
INTEGRAL=	286.28	
FROM	7.33 TO	7.27 PPM
INTEGRAL=	111.33	
FROM	7.23 TO	7.15 PPM
INTEGRAL=	99.37	
FROM	3.73 TO	3.67 PPM
INTEGRAL=	273.33	
FROM	1.46 TO	1.40 PPM
INTEGRAL=	985.13	

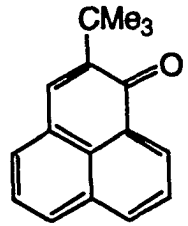
K2 . 451 15U 20JUN89
SEP. 2ND 451



28

1-Methyl-3-(1-methylethyl)-2(1*H*)-quinolininone

KA111 . 423 ISU 24APR89
423A 3RD SPOT RT.18.2.

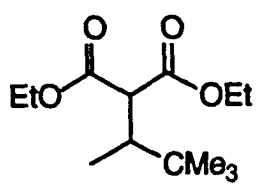


29

2-(1,1-Dimethylethyl)-(1*H*)-phenalen-1-one

FROM	7.44	TO	7.37 PPM
INTEGRAL=	1.00		
FROM	8.43	TO	8.35 PPM
INTEGRAL=	.82		
FROM	8.16	TO	7.88 PPM
INTEGRAL=	2.89		
FROM	7.88	TO	7.66 PPM
INTEGRAL=	2.17		
FROM	7.46	TO	7.38 PPM
INTEGRAL=	1.14		
FROM	1.47	TO	1.38 PPM
INTEGRAL=	8.27		

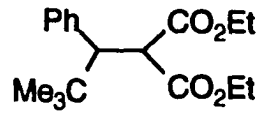
KA1 . 634 ISU 23DEC89
SEP.



32

Diethyl (1,2,2-trimethylpropyl)malonate

KB2 . 907 ISU 19MAY90
SEP.

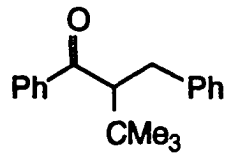


33

FROM	4.01	TO	3.92 PPM
INTEGRAL=	100.00		
FROM	4.33	TO	4.13 PPM
INTEGRAL=	199.19		
FROM	3.[illegible]	TO	3.04 PPM
INTEGRAL=	197.45		
FROM	3.52	TO	3.39 PPM
INTEGRAL=	94.94		
FROM	7.25	TO	7.18 PPM
INTEGRAL=	524.56		
FROM	1.34	TO	1.24 PPM
INTEGRAL=	345.86		
FROM	.98	TO	.83 PPM
INTEGRAL=	867.26		
FROM	.83	TO	.74 PPM
INTEGRAL=	337.76		

Diethyl (2,2-dimethyl-1-phenylpropyl)malonate

Ki . 753 C. 05APR90
SEP.

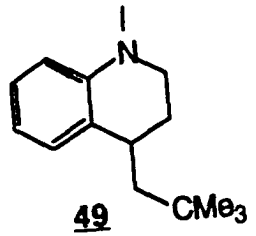


35

2-Benzyl-3,3-dimethyl-1-phenyl-1-butanone

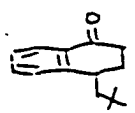
4-(2,2-Dimethylpropyl)-1-methyl-1,2,3,4-tetrahydroquinoline

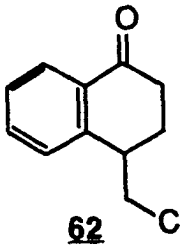
SEP. 87% PURE



49

KB1 . 650 ISU 11JAN90
SEP.



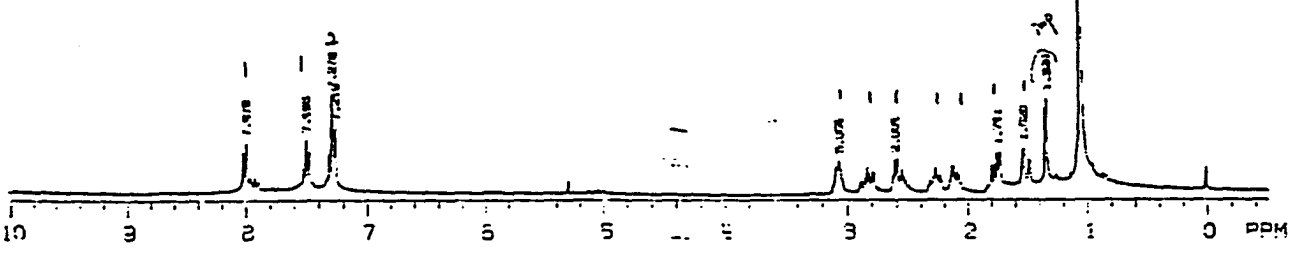


62 CMe_3

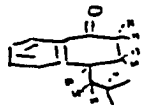
N-(1,1-dimethylethoxy)-*N*-(1,1-dimethylethyl)aniline

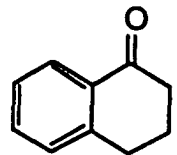
FROM 3.15 TO		2.99 PPM
INTEGRAL = 100.00		
FROM 2.91 TO		2.71 PPM
INTEGRAL = 100.40		
FROM 2.64 TO		2.47 PPM
INTEGRAL = 141.86		
FROM 2.35 TO		2.19 PPM
INTEGRAL = 103.60		
FROM 2.17 TO		2.03 PPM
INTEGRAL = 109.79		
FROM 1.81 TO		1.69 PPM
INTEGRAL = 132.80		
FROM 1.57 TO		1.44 PPM
INTEGRAL = 175.63		
FROM 1.39 TO		1.29 PPM
INTEGRAL = 192.84		
FROM 1.13 TO		.98 PPM
INTEGRAL = 1069.44		
FROM 8.03 TO		7.96 PPM
INTEGRAL = 113.84		
FROM 7.53 TO		7.43 PPM
INTEGRAL = 146.16		
FROM 7.34 TO		7.21 PPM
INTEGRAL = 252.32		

8.04 TO		7.96 PPM
INTEGRAL = 100.00		
FROM 7.52 TO		7.43 PPM
INTEGRAL = 127.54		
FROM 7.32 TO		7.22 PPM
INTEGRAL = 217.54		



KB . 663 ISU 29JAN90
SEP.





63 $CHMe_2$

FROM 8.06	TO	7.97 PPM
INTEGRAL= 108.89		
FROM 7.54	TO	7.42 PPM
INTEGRAL= 114.76		
FROM 7.34	TO	7.21 PPM
INTEGRAL= 249.39		
FROM 3.07	TO	2.92 PPM
INTEGRAL= 99.54		
FROM 2.84	TO	2.68 PPM
INTEGRAL= 99.93		
FROM 2.65	TO	2.31 PPM
INTEGRAL= 115.72		
FROM 2.35	TO	2.14 PPM
INTEGRAL= 121.84		
FROM 2.08	TO	1.95 PPM
INTEGRAL= 124.78		
FROM 1.82	TO	1.39 PPM
INTEGRAL= 543.68		
FROM 1.32	TO	1.23 PPM
INTEGRAL= 153.89		
FROM 1.04	TO	.92 PPM
INTEGRAL= 743.88		

3,4-Dihydro-4-(2-methylpropyl)-1(2*H*)-naphthalenone

6