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Deoxygenation reactions of 1-alkenyl nitro compounds with ethyl phosphites and alkylmercury iodides: promotion of reactions of tertiary-butylmercury halides with [alpha],[beta]-unsaturated nitriles in the presence of proton donors

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GENERAL INTRODUCTION

The Michael addition reaction is one of the most synthetically useful reactions.[1] The reaction of 1-nitro-1-cyano-2-phenylethylene with amines in ethanol to form $PhCH[CH(CN)NO_2]_2$ instead of the expected normal adduct is an interesting exception reported by Demireva et al.[2] The reactions of 1,1-diaryl-2-nitroethylene with *tert*-butoxide ion in *tert*-butyl alcohol to yield 1,3-dinitro-2,2-diarylpropane and of 9-(dinitromethylene)-fluorene with secondary amines in acetonitrile to yield 9,9-bis(dinitromethyl)fluorene are consistent with this exception.[3] In contrast to the reactions listed above, we have found that RS^- reacts with $Ph_2C{=}C(SPh)NO_2$ in Me_2SO to form $Ph_2C{=}CHSR$ via conversion of the initial Michael-type adducts into $Ph_2C(SR)CH{=}NO_2^-$ and $Ph_2C{=}CHNO_2$.[4] In a similar fashion, reaction of $(EtO)_2PO^-$ with $Ph_2C{=}C(SPh)NO_2$ forms products from $Ph_2C[P(O)(OEt)_2]CH(SPh)NO_2$ including $Ph_2C[P(O)(OEt)_2]CH_2NO_2$, its Nef reaction product $Ph_2C[P(O)(OEt)_2]CHO$, or a Perkow-type reaction product $Ph_2C[P(O)(OEt)_2]CN$.[4] However, reaction of $Ph_2C{=}C(SPh)NO_2$ with $(EtO)_2PO^-$ also formed heterocyclic compounds such as azirines, aziridines and indoles which are most reasonably formulated as arising from the deoxygenation of the nitro alkene to the nitroso compound followed by further reaction with $(EtO)_2PO^-$.

Similar results have been observed in the reaction $Ph_2C{=}C(Y)NO_2$ (Y= H, CH_3, NO_2, SBu-*t*) and cis-α-nitrostilbene with $(EtO)_2PO^-$. The deoxygenation of nitro and nitroso compounds to generate nitrenes

by tervalent phosphorous reagents has been previously reported.[5] High yields of indoles or in one case an aziridine have been observed when $Ph_2C=C(Y)NO_2$ reacted with $(EtO)_3P$ or $(EtO)_2POH$ at the temperature of 150 °C.[4] The indoles are believed to be formed from intermediate azirine via thermal conversion to the nitrenes.

The reaction of Grignard reagents with nitroarenes has received considerable attention in the past.[6-14] The mixture of *t*-BuHgI and KI in Me_2SO will reduce enolyl redicals to enolate anion[15] in a process postulated to involve the ate-complex, *t*-$BuHgI_2^-$. This system also photochemically deoxygenates nitroalkenes or aromatic nitro compounds to yield products mainly derived from the resulting nitroso compounds. To support this first example of the deoxygenating of nitro and nitroso compounds by alkylmercury halides, a variety of reaction products will described and their formation described mechanistically as arising from the sequence, $Ar_2C=C(Y)NO_2 \rightarrow Ar_2C=C(Y)N(OBu\text{-}t)OHgI \rightarrow Ar_2C=C(Y)NO \rightarrow Ar_2C=C(Y)N(OBu\text{-}t)HgX \rightarrow Ar_2C=C(Y)\ddot{N} \rightarrow Ar_2C=C(Y)N(Bu\text{-}t)HgI$. (Y= H, Me, Ph, SPh, SBu-*t*).

The photostimulated addition of alkylmercury chlorides to substituted ethylenes has been studied by Russell et al.[16] α,β-Unsaturated nitriles and 2-(1-alkenyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazines react with alkylmercury hailides upon photolysis to give low yield of monoalkylated, dimer or oligomer products. By using the proton donor PTSA(*p*-toluenesulfonic acid) in the presence of KI, the yields of the monoalkylated products were greatly increased,

presumably from electron transfer from *t*-$BuHgI_2^-$ to the protonated adduct radical.[17] Evidence will be presented for the formation of intermediate ketenimine from this process.

Explanation of dissertation format

The format of this dissertation is an alternate format as described in the Thesis Manual. It consists of two papers (Part I and Part III). The style of the papers are according to the American Chemical Society. Part I has been mainly published in the Journal of Organic Chemistry (Ref 4) while some the results of Part III have appeared as a Communication to the Editor of the Journal of the American Chemical Society (Ref 17). References cited in the General Introduction and General Summary are listed after the General Summary.

PART I. ADDITION, SUBSTITUTION AND DEOXYGENATION REACTIONS OF α-PHENYL-β-NITROSTYRENES WITH THE ANIONS OF THIOLS AND DIETHYL PHOSPHITE; FORMATION OF INDOLES BY REACTION WITH ETHYL PHOSPHITES

Addition, substitution and deoxygenation reactions of α–phenyl-β-nitrostyrenes with the anions of thiols and diethyl phosphite; Formation of indoles by reaction with ethyl phosphites

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ABSTRACT

Reactions of excess RS^- (R=Ph, *t*-Bu) with $Ph_2C=C(SPh)NO_2$ in Me_2SO form $Ph_2C=CHSR$ via conversion of the initial Michael-type adducts into $Ph_2C(SR)CH=NO_2^-$ and $Ph_2C=CHNO_2$. In a similar fashion, reaction of $(EtO)_2PO^-$ with $Ph_2C=C(SPh)NO_2$ forms initially $PhSP(O)(OEt)_2$ and $Ph_2C[P(O)(OEt)_2]CH=NO_2^-$ which upon acidic work-up will yield the nitroalkane or the Nef reaction product, $Ph_2C[P(O)(OEt)_2]CHO$. The reaction of $(EtO)_2PO^-$ with $Ph_2C=C(SPh)NO_2$ also produces $Ph_2C[P(O)(OEt)_2]CN$ via a Perkow-type reaction of the Michael adduct to yield, $Ph_2[P(O)(OEt)_2]CH=N(O)OP(O)(OEt)_2$ as an intermediate. The nitrile is also formed from $Ph_2C[P(O)(OEt)_2]CH(NO_2)_2$ with $(EtO)_2PO^-$ in $(EtO)_2P(O)H$ or Me_2SO at 30 °C and in >95% yield by the reaction of $(EtO)_3P$ with $Ph_2[P(O)(OEt)_2]CH(NO_2)_2$ at 150 °C. Reaction of $Ph_2C=C(R)NO_2$ (R=H, CH_3) or $Ph_2C[P(O)(OEt)_2]CH_2NO_2$ with excess $(EtO)_2PO^-$ in Me_2SO or $(EtO)_2P(O)H$ forms 3-(diethoxyphosphinyl)-2,2-diphenylaziridine (R=H) and 3-(diethoxyphosphinyl)-3-methyl-2,2-diphenylaziridine (R=Me) by a process postulated to involve $Ph_2C=C(R)N(O^-)OP(O)(OEt)_2$, $Ph_2C=C(R)NOP(O)(OEt)_2^-$ and 2,2-diphenyl-2*H*-azirine or 2,2-diphenyl-3-methyl-2*H*-azirine. Similarly, $Ph_2C=C(SBu\text{-}t)NO_2$ and $(EtO)_2PO^-$ give 3-(*tert*-butylthiyl)-2,2-diphenyl-2*H*-azirine in Me_2SO or 2-(*tert*-butylthiyl)-3-phenylindole in $(EtO)_2P(O)H$ solution. Reaction of (*E*)-$PhHC=C(Ph)NO_2$ (cis-α-nitrostilbene) with $(EtO)_2PO^-$ in Me_2SO forms diethyl(2-nitro-1,2-diphenylethyl)phosphonate while in

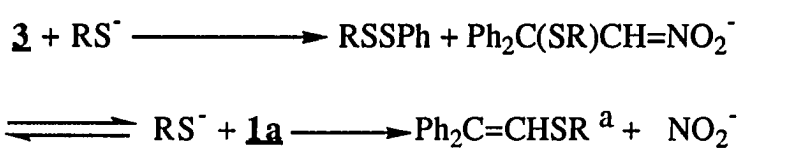
EtOH at 70 °C the products are 3-(diethoxyphosphinyl)-1-hydroxy-2-phenylindole and 3-(diethoxyphosphinyl)-2-phenylindole. Deoxygenation of $Ph_2C=C(X)NO_2$ to form 2-X-3-phenylindoles occurs in high yield at 150 °C in $(EtO)_3P$ with X=H, Me, PhS, PhO or *t*-BuS while 2-nitro-3-phenylindole is formed from $Ph_2C=C(NO_2)_2$ in $(EtO)_2P(O)H$ at 150 °C. Reaction of (*E*)-$PhHC=C(Ph)NO_2$ with $(EtO)_3P$ at 150 °C for 3 h forms $PhCH=C(NHPh)P(O)(OEt)_2$ ((*E*) and (*Z*) diethyl(1-anilino-2-phenylvinyl)phosphonate) and a trace of 2-phenylindole.

INTRODUCTION

Reaction of 1,1-dinitro-2,2-diphenylethylene (**1d**) with one equivalent of $(EtO)_2P(O)^-$ (P^-) in Me_2SO gives upon acidification a quantitative yield of the adduct **2d**.[1] The adduct **2a** is also formed from 2-nitro-1,1-diphenylethylene with P^- in the presence of $(EtO)_2P(O)H$ (PH). However, reaction of one equiv of RS^- with **1d** in Me_2SO lead to the displacement of a nitro group forming **1b** or **1c** in high yield[1] while **1a** is converted to $Ph_2C{=}CHSR$.

We were initially drawn to a further study of these systems by the observation that excess PhS^- reacted slowly but essentially quantitatively with **1b** to form $Ph_2C{=}CHSPh$ and PhSSPh. Further work supported the premise that this denitrofication proceeded by the formation of the adduct **3a** followed by nucleophilic attack at the thiophenyl substituent to form the nitronate anion, Scheme I.[2]

Scheme I



[a]The possibilty exists that $Ph_2C(SPh)CH{=}NO_2^-$ might be converted into $Ph_2C{=}CHSPh + NO_2^-$ in an intramolecular reaction.[1]

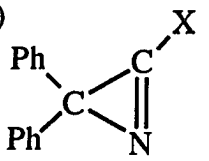
(1)		(2)		(3)	
$Ph_2C=C(X)NO_2$		$Ph_2C[P(O)(OEt)_2]CH(X)NO_2$		$Ph_2C(SR)CH(SPh)NO_2$	
1a	X=H	**2a**	X=H	**3a**	R=Ph
1b	X=PhS	**2b**	X=PhS	**3b**	R=*t*-Bu
1c	X=*t*-BuS	**2c**	X=*t*-BuS		
1d	$X=NO_2$	**2d**	$X=NO_2$		
1e	$X=CH_3$				
1f	X=PhO				

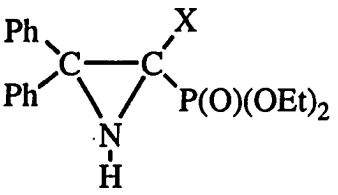
In a similar fashion, the reaction of P^- with **1b** initially forms mainly **2a** and $PhSP(O)(OEt)_2$ via nucleophilic attack upon the sulfur atom in the adduct **2b**. However, we found that the reactions of excess P^- with the α-phenyl-β-nitrostyrene derivatives **1** were complex and could yield heterocyclic products such as **4-6** or the nitriles **7**. This prompted us to examine the deoxygenation of **1** with $(EtO)_3P$ under conditions where nitroaromatics are converted to nitrenes.[3] At 150 °C the indoles **6a-c** are formed in high yield from **1a-f**, possible via the azirines[b] **4a-f**,[4-7] while **6d** is formed from **1d** in $(EtO)_2P(O)H$.

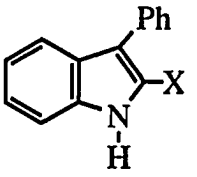
---

[b]The thermal conversion of 2*H*-azirines to indoles is usually formulated to involve the nitrene as an intermediate.[4,5] In general, thermal processes leading to vinylnitrenes proceed by initial formation of 2*H*-azirines.[6,7]

cis-α-Nitrostilbene also leads to indoles **8a-c** and compound **9** under these conditions in Me_2SO or EtOH. The formation of 2-alkyl-3-(diethoxyphosphinyl)-N-hydroxyindoles (analogous to **8c**) has been previously reported for the reaction of $PhCH=C(R)NO_2$ with $(EtO)_2P(O)H/K_2CO_3$ in EtOH.[8] The formation of the indole **8a** from (*E*)-$PhCH=C(Ph)NO_2$ has also been reported to occur upon deoxygenation with $(EtO)_3P$.[9]

(**4**) 

(**5**) 

(**6**) 

4 a	X=H	**5 a**	X=H	**6 a**	X=H
4 b	X=PhS	**5 b**	X=CH_3	**6 b**	X=PhS
4 c	X=*t*-Bus			**6 c**	X=*t*-BuS
4 d	X=NO_2			**6 d**	X=NO_2
4 e	X=CH_3			**6 e**	X=CH_3
4 f	X=PhO			**6 f**	X=PhO

β-Nitrostyrene does not form indole[c] under these conditions[10,11] and at ambient temperatures yield products derived from the addition of $(EtO)_3P$ at the alpha carbon atom,[12] a process apparently hindered by an α-phenyl substituent.

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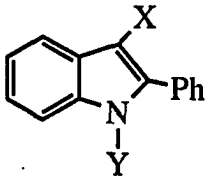
[c]Pyrolysis of 2-phenyl-2*H*-azirine forms $PhCH_2CN$ and indole in approximately equal amounts.[4,11]

(7) $Ph_2C(X)CN$ (8)

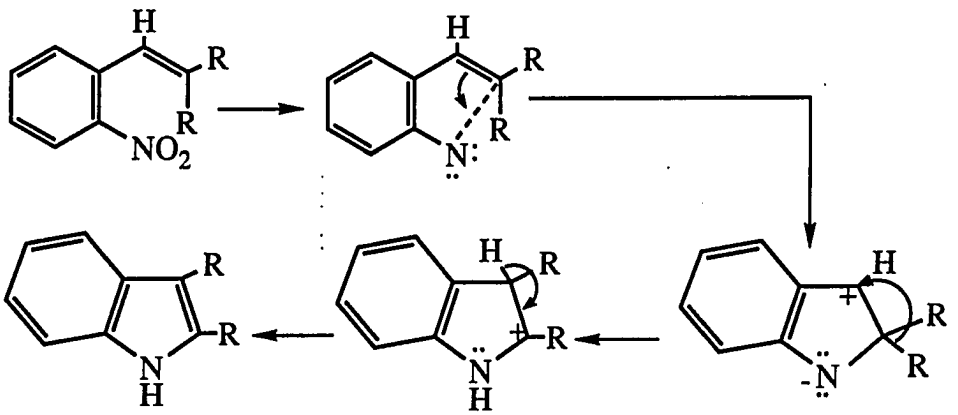


7a	X=H	8a	X=H, Y=H
7b	X=PhS	8b	X=P(O)(OEt)2, Y=H
7c	X=*t*-BuS	8c	X=P(O)(OEt)2, Y=OH
7d	X=P(O)(OEt)2		

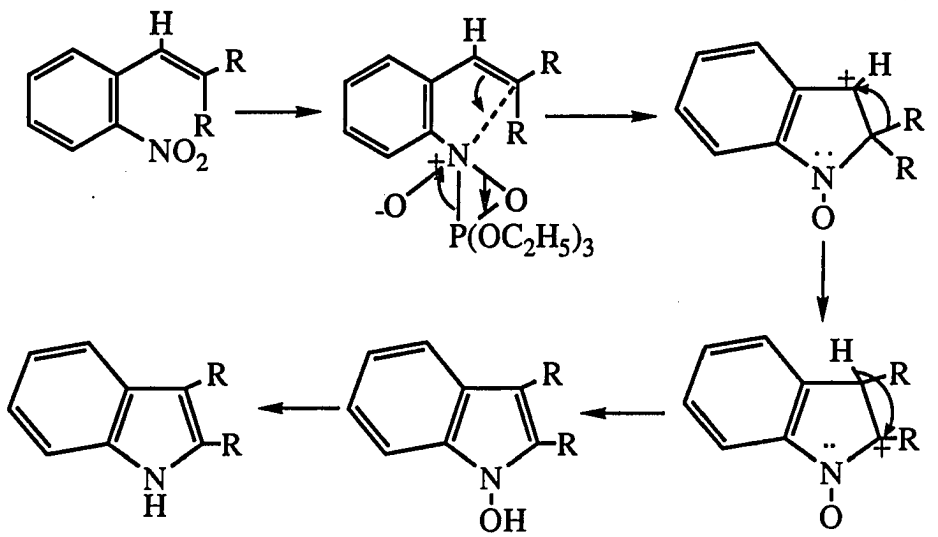
(9) PhCH=C(NHPh)P(O)(OEt)2

There are no other examples of the conversion of β-nitrostyrene derivatives into indoles except for references 8 and 9. The deoxygenation of *o*-nitrostyrenes by heating with $(EtO)_3P$ is well known.[13] Sundberg and Yamazaki suggested two possible mechanisms for these processes, the nitrene mechanism of Scheme II and the N-hydroxyindole mechanism of Scheme III.

Scheme II



Scheme III



RESULTS AND DISCUSSION

Reactions of nucleophiles with 1-nitro-2,2-diphenyl-1-(phenylthiyl)ethylene

Compound **1b** reacted slowly with 5 equiv of PhS^- in Me_2SO to form $Ph_2C{=}CHSPh$ (94% isolated yield) and PhSSPh or with excess *t*-BuS^- to form $Ph_2C{=}CHSBu\text{-}t$ (88% isolated yield). The reactions are neither stimulated by sunlamp irradiation nor retarded by 5-10% of $(t\text{-}Bu)_2NO\cdot$ or $p\text{-}O_2NC_6H_4NO_2$. The only effect of exposure to air is an increased yield of PhSSPh. It thus appears that the reaction of **1b** with RS^- in Me_2SO is an ionic process.[14] Furthermore, in the early stages of the reaction, $Ph_2C{=}CHNO_2$ can be detected as intermediate (Fig. 1). This supports the process of Scheme I (R=Ph or *t*-Bu). The nitro-substitution product [$Ph_2C{=}C(SPh)_2$] was not observed in the reaction of PhS^- with **1b** although it was independently shown to persist under the reaction conditions.

No reaction was observed between PhS^- and **1c**, in this case, the intermediate adduct [$Ph_2C(SPh)CH(SBu\text{-}t)NO_2$] may not be formed, or if formed at a low equilbrium concentration, the adduct may be sterically hindered to nucleophilic attack by PhS^-. The adduct **3a** could not be detected by GCMS in the CH_2Cl_2 extracts of the hydrolysis products from the reaction of **1b** with a deficiency of PhSK/PhSH in Me_2SO, THF, DMF or EtOH. In Me_2SO apparently **3a** is formed slowly but reacts rapidly with PhS^- according to Scheme I.

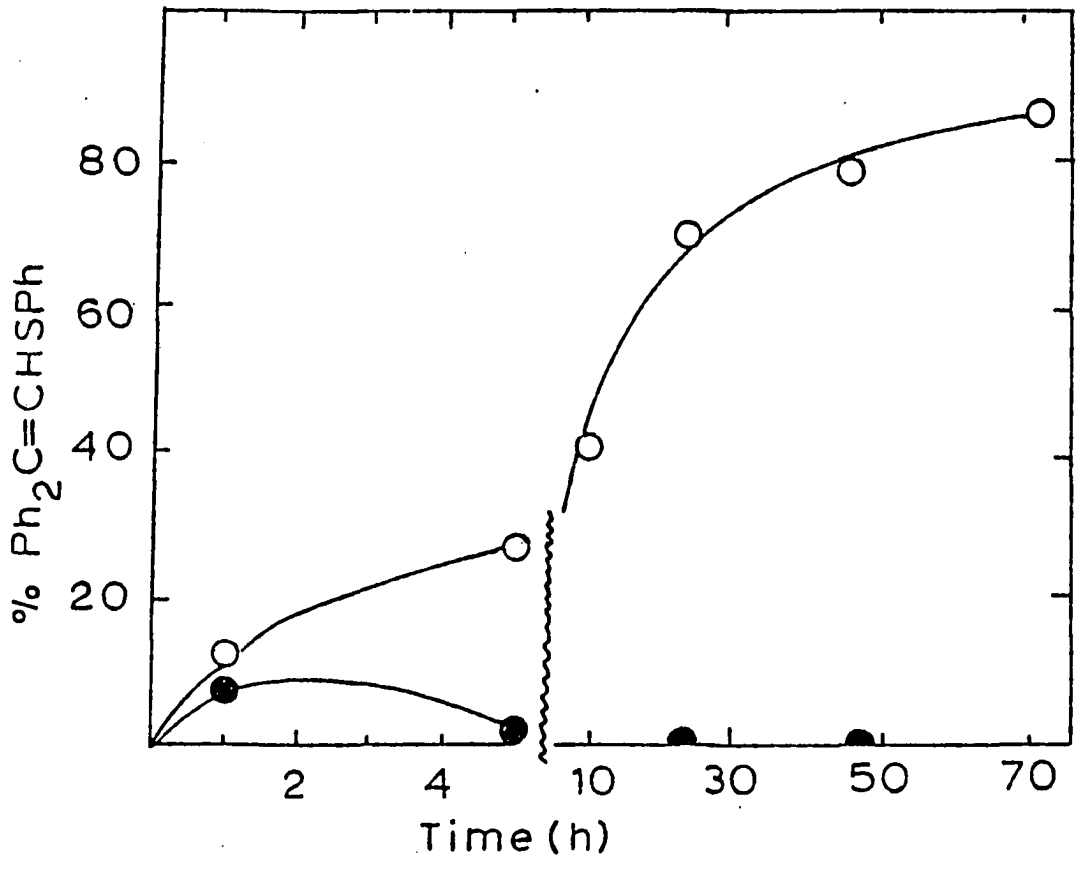


Fig. 1 Reaction of **1a** (initially 0.02 M) with PhSK (0.10 M) in Me_2SO at 25 °C; O, % Ph_2C=CHSPh; ●, % Ph_2C=$CHNO_2$

The reaction of 5 equiv. of P^- with **1b** in Me_2SO gave as major products $PhSP(O)(OEt)_2$, **2a**, **7d** and **5a** (Table 1) with **5a** increasing at the expense of **2a** at higher concentrations of reactants or longer reaction times. Reaction of **2a** with excess P^- in Me_2SO formed **5a** but not **7d**. Thus, the major initial products from **1b** are **2a** and **7d**, both of which can be reasonably formulated by further reactions of the initially formed adduct **2b**. Initially **2a** greatly predominates over **7d** consistent with preferred nucleophilic attack upon **2b** to form the nitronate anion. In PH solution the reaction of excess P^- with **1b** occurs more rapidly. Hydrolysis with brine after a 2 min reaction period gave a 50% yield of the Nef reaction product $Ph_2C[P(O)(OEt)_2]CHO$ expected from $Ph_2C[P(O)(OEt)_2]CH{=}NO_2H$.

Minor products observed in the reaction of **1b** with P^- in Me_2SO include **1a**, **7a**, PhSSPh, the indole **6b** and at longer reaction times the indole **6a**. In moist Me_2SO, Ph_2CO is formed from the hydrolysis of **1b** with traces of $Ph_2C(NH_2)COOEt$ observed. These products suggest minor reaction pathways leading to **7b** (converted to **7a** by P^-) and the azirine **4b** (converted to the indole **6b** or to $Ph_2C(NH_2)COOEt$).

Reactions leading to $Ph_2C[P(O)(OEt)_2]CN$

The formation of the nitrile **7d** as a minor product in the reaction of **1b** with P^- can be rationalized as arising from a Perkow-type reaction of the adduct **2b** to form **10** followed by deoxygenation and

Table 1. Reactions of $Ph_2C=C(SPh)NO_2$ (**1b**) with $(EtO)_2POK$ in Me_2SO at 25-30 °C

Reactants (M)		Time (h)	Products (%)[a]				
1b	P^-		**2a**	**7d**	**5a**	$PhSP(O)(OEt)_2$	Others
0.006	0.03	0.5	37	7	tr	41	[b]
0.006	0.03	1.0	37	10	tr	43	[c]
0.006	0.03	24	17	11	+	37	[d]
0.072	0.36	2.0	15[e]	9[e]	30[e]	60	**6a** (tr)
0.054	0.27	17	+	+	50	+	

[a]By GC using biphenyl as an internal standard.

[b]**7a** (tr), **6b** (tr), Ph_2S_2 (7%), $Ph_2C=CHSPh$ (6%), **1a** (2%).

[c]**7a** (tr), **6b** (tr), Ph_2S_2 (4%), $Ph_2C=CHSPh$ (6%), **1a** (3%).

[d]**7a** (tr), **6b** (tr), Ph_2S_2 (4%), $Ph_2C=CHSPh$ (8%), **1a** (3%).

[e]Isolated by column chromatography.

elimination of $(EtO)_2PO_2H$[15,d] (Scheme IV, X=PhS). There are several literature precedents for such reactions of α-substituted nitroalkanes.

Scheme IV

$$\underline{2} + P^- \longrightarrow Ph_2C[P(O)(OEt)_2]CH(X)N(O^-)OP(O)(OEt)_2$$

$$\longrightarrow X^- + Ph_2C[P(O)(OEt)_2]CH{=}N(O)OP(O)(OEt)_2$$

$$\underline{10}$$

$$\underline{10} \xrightarrow[-(EtO)_2PO_2H]{-[O]} \underline{7\ d}$$

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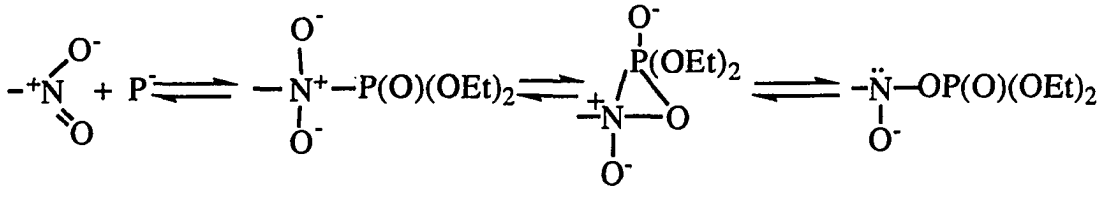
[d]For brevity, intermediates are shown in which phosphorous is bonded only to the oxygen atom of a nitro or nitroso group. Initial attack by P^- may well occur at nitrogen followed by rearrangement of i to ii and iii. A similar structure can be written for attack of $(EtO)_3P$. Although the conversion of a nitro group to a nitroso group can be readily rationalized from ii or iii, the Perkow reaction of **2b** or **2d** and azirine formation from **1**, is much better accomodated by iii and the analogous deoxygenated species $-NOP(O)(OEt)_2^-$.



i ii iii

with phosphorus nucleophiles. Thus reaction 1 occurs readily,[16] and the same product is formed

$$Me_2C(NO_2)_2 + P^- \xrightarrow{Me_2SO} [Me_2C{=}N(O)OP(O)(OEt)_2] \xrightarrow[-[O]]{} Me_2C{=}NOP(O)(OEt)_2 \qquad (1)$$

from the Perkow/Arbuzov reaction of $(EtO)_3P$ with $Me_2C(Cl)NO_2$.[17] In these reactions the intermediate nitronic phosphate is deoxygenated to the oximino phosphate by oxygen atom transfer to $(EtO)_3P$ or P^-. However, in the case of **10** the timing of the deoxygenation and elimination steps is not clear since an E2 elimination from **10** would produce a nitrile oxide $[Ph_2C[P(O)(OEt)_2CNO]$ which would be readily deoxygenated to the nitrile.[18] However, the reaction of $PhCH{=}NO_2K$ with $(EtO)_2PCl$ in ether yields PhCN by a process not involving the nitrile oxide. The initially formed $PhCH{=}CN(O)OP(OEt)_2$ rearranges to $PhCH{=}CNOP(O)(OEt)_2$ which eliminates $(EtO)_2PO_2H$. Reaction of $Me_2C{=}NO_2^-$ with $(EtO)_2PCl$ yields $Me_2C{=}NOP(O)(OEt)_2$.[30]

Reactions of Ph_3P with α-substituted 2°-nitroalkanes also occurs by a Perkow-type process. The reaction of $RCH(Br)NO_2$ (R=Me, Et) with Ph_3P in PhH at 0-5 °C yields the isolable $HON{=}C(R)PPh_3^+Br^-$ which is hydrolyzed to the nitrile. A Perkow-type process has been postulated in the reaction of Ph_3P with $ArCH{=}C(Br)NO_2$ (Ar=Ph, *p*-MeC_6H_4) in MeOH to yield $ArCH{=}C{=}N(O)OPPh_3^+$ which after

deoxygenation reacts with Ph_3P to form $Ph_3P{=}C(Ar)CN$ and a 2*H*-azirine which can methanolized to $PhC(OMe){=}NCH_2PPh_3^+Br^-$.[31]

The reaction of **2d** with 5-10 equiv of P^- also forms the nitrile **7d** in Me_2SO or PH solution. However, the nitrile is now accompanied an equal amount of $Ph_2CHP(O)(OEt)_2$. Both products can be explained by Scheme IV (with $X{=}NO_2$) if elimination of NO_2^- and $Ph_2CP(O)(OEt)_2^-$ are competitive. (With the better leaving group PhS the elimination of $Ph_2CP(O)(OEt)_2^-$ was not detected.) In the reaction of **2d** (0.3 M) with 5 equiv of P^- in PH an intermediate could be detected by GCMS at short reaction times. This intermediate gave m/z=345 (3%) and 208 (100%) and is consistent with the nitrile oxide, $Ph_2C[P(O)(OEt)_2]CNO$ (fragmentation forms Ph_2CCNO^+ as the base peak).

In hope of improving the yield of **7d**, the reaction of **2d** with $(EtO)_3P$ and $(EtO)_2POH$ at 150 °C was examined (Table 2). The reaction with $(EtO)_3P$ was particularly clean leading to **7d** in >95% yield in 1 h. Presumably the reaction follows Scheme IV with $X{=}NO_2$ and $(EtO)_3P$ in place of P^-. If this is so, only NO_2^- is eliminated from the intermediate $Ph_2C[P(O)(OEt)_2]CH(NO_2)N(O^-)OP(OEt)_3^-$, possibly because of an interaction between the nitro oxygen atom and the positively charged phosphorus atom.

Nitroalkanes such as $PhCH_2CH_2NO_2$ are known to undergo deoxygenation/dehydration with $(EtO)_3P$ at elevated temperature to yield the nitrile.[19] However, **2a** with $(EtO)_3P$ or pH at 150 °C formed

Table 2. Reaction products from $Ph_2C[P(O)(OEt)_2]CH_2NO_2$ (**2a**) or $Ph_2C[P(O)(OEt)_2]CH(NO_2)_2$ (**2d**) in ethyl phosphite solution at 150 °C

Substrate[a]	Solvent	Time (h)	Product (%)[b]	
			7d	$Ph_2CHP(O)(OEt)_2$
2d	$(EtO)_3P$	1	>95	c
2d	$(EtO)_3P/(EtO)_2P(O)H$[d]	1	>95	c
2d	$(EtO)_2P(O)H$	1	14	3
2a	$(EtO)_3P$	1	23	26[e]
2a	$(EtO)_3P/(EtO)_2P(O)H$[d]	1	22	76
2a	$(EtO)_2P(O)H$	1	32	8
2a	$(EtO)_2P(O)H$	13	14	19

[a]0.3 mmol of substrate in 1 mL of the phosphite.

[b]By GC using biphenyl as an internal standard.

[c]Not observed.

[d]1:1 volume ratio (3.9 mmol of $(EtO)_2P(O)H$ and 2.9 mmol of $(EtO)_3P$).

[e]7% of **5a** observed.

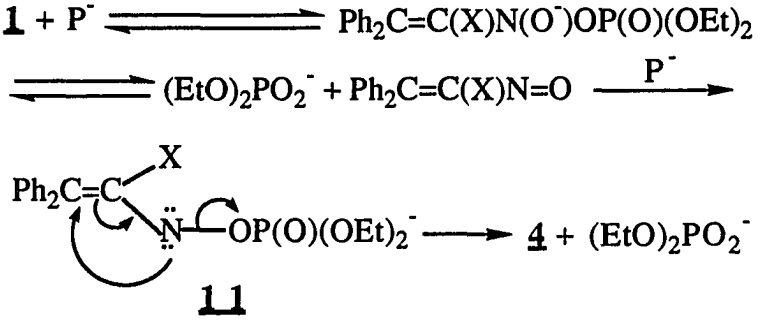
considerable amounts of $Ph_2CHP(O)(OEt)_2$ in addition to **7d**, presumably from the elimination of $Ph_2CP(O)(OEt)_2^-$ from the intermediate $Ph_2C[P(O)(OEt)_2]CH_2N(O^-)OP(OEt)_3^+$. Table 2 also presents evidence that suggest that **7d** can be slowly converted to $Ph_2CHP(O)(OEt)_2$ by reaction with PH at 150 °C (compare entries 6 and 7).

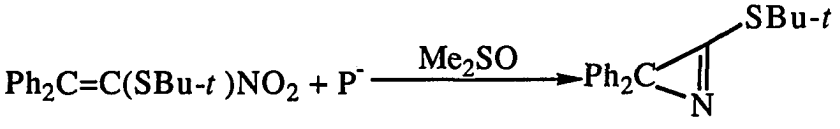
Conversion of $Ph_2C=C(X)NO_2$ into 2*H*-azirines and 2-X-3-phenylindoles

The reaction of one equiv of P^- with $Ph_2C=CHNO_2$ establishes an equilbrium with **2a**. With **1a**=0.5 M, hydrolysis gave **2a** in 7% yield after 144h in Me_2SO or in 37% after 1h in PH. In PH solution **2a** was accompanied by significant amount of the aziridine **5a**. With excess P^- in Me_2SO or PH, the aziridine is the major product from either $Ph_2C=CHNO_2$ or the adduct **2a**. Thus, in 5 h with 10 equiv of P^- in PH, a 90% yield of **5a** was isolated from a reaction initially 0.14 M in **2a** while in Me_2SO **2a** gave a yield of 50% in 168h. Formation of the nitrile **7d** was not observed in either solvent. The formation of **5a** seems most reasonably formulated by attack of P^- upon the nitro group of **1a** (Scheme V with X=H) to yield the azirine **4a** which is trapped by P^- to give the aziridine **5a**. With 5 equiv P^- and 5 equiv PH in Me_2SO, the aziridine **5b** (51%) is the major product formed from **1e** ($Ph_2C=C(CH_3)NO_2$) in 2 h. Support for the mechanism of Scheme V was provided by the observation that in Me_2SO the major

product formed from 1c and excess P^- was the azirine 4c (Reaction 2). Compound 4c was isolated in 49% yield (plus 9% of the hydrolysis product $Ph_2C(OH)C(SBu\text{-}t)=NH$) after a 2 h reaction period in Me_2SO following the dropwise addition of 1c to 10 equiv. of 0.25 M P^-. Also

Scheme V



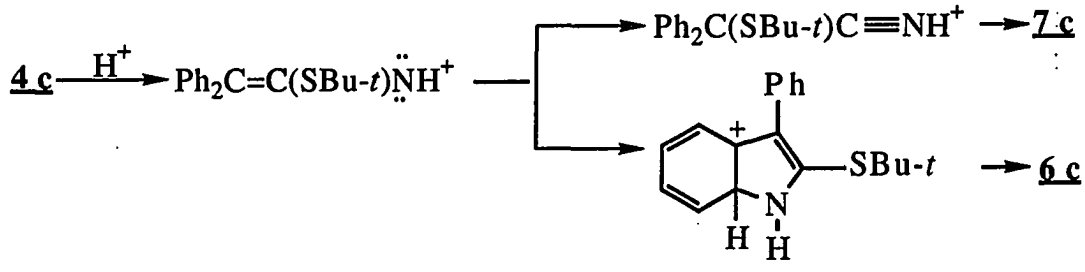


(2)

observed were traces of Ph_2CHCN(7a) and t-$BuSP(O)(OEt)_2$. In PH as solvent 4c appeared to be the major initial product (by GC) but it was rapidly converted into a 7:1 mixture of the indole 6c and the nitrile 7c, Scheme VI. The indole was isolated in 53% yield from a 30 min reaction of 1c with 5 equiv of P^- in PH. In this reaction after 2 min, GC analysis indicated a ratio of 4c:6c of ~5:1 but after 30 min, 4c was not detected. The nitrile 7a and a trace of t-$BuSP(O)(OEt)_2$ were also observed but the yield of 7a did not increase after the initial 30 min

reaction period. In this case, 7a in not formed by nucleophilic attack upon 7c.[e]

Scheme VI



The contrasting behavior of 1b and 1c in reaction with P^- is easily understand in terms of the adduct 2. With 1b the adduct is formed and undergoes competing reactions with P^- by Schemes I and IV with only a minor contribution from Scheme V. With 1c, either the adduct 2c is not formed, or if it is present in equilbrium with 1c the adduct fails to react with P^- by Scheme I (steric) or by Scheme IV (*t*-BuS^- is a poor leaving group than PhS^-). The predominant reaction of 1c thus follows Scheme V.

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[e]Alternatively, Scheme V, with X=H could be entered by rearrangement of $Ph_2C[P(O)(OEt)_2]CH=NO_2^-$ to $Ph_2C=CHN(O^-)OP(O)(OEt)_2$. Reactions which form 2a in low yield, e.g. $[P^-]=[1a]=0.05$ M in Me_2SO, give very little of 5a.

In view of the results obtained in the reaction of P^- with **1a-1c** it seemed reasonable that azirines would be formed from reactions with $(EtO)_3P$ (i.e. via Scheme V with $(EtO)_3P$ in place of P^-). We thus examined the reaction of **1** with $(EtO)_3P$ at temperatures where 2-phenyl-2*H*-azirines are known to isomerize to indoles (Table 3).

Reaction of **1d** with $(EtO)_3P$ gave a complex set of reaction products. However, with 4 equiv of PH for 30 min at 150 °C, **6d** was formed in 52% yield (12% of recovered **1d**). Also observed were **7d** (3%), **6a** (3%) and **1a** (2%). Reaction for 3 h gave **6a** and **6d** in about equal amounts suggesting a denitrofication of **6d**. The low yield of **7d** indicated that addition of PH to **1d** was not important since under the reaction conditions the adduct **2d** forms **7d** in significant amounts (Table 2). Reaction of **1b** or **1c** with PH at 150 °C yield a complex set of reaction including products formed from further reactions of Ph_2CHCN (e.g. $Ph_2CHC(O)SBu$-*t* , $Ph_2CHC(OEt)=NH$). With **1c** 2-(ethylthiyl)-3-phenylindole was formed, presumably by dealkylation/alkylation of **6c**.

The source of **7a** in the reactions of **1b** or **1c** with P^- in Me_2SO or PH is unclear. Rearrangement with elimination of $(EtO)_2PO_2^-$ from **11** (X=PhS) to form **7b** which could be the precursor to **7a** is a possibilty but this process seems to be excluded with X=*t*-BuS. Significant amounts of **7a** were only observed in PH solution. This suggest a sequence involving the protonation of **11** followed by the loss of the elements RS and $(EtO)_2PO_2$.

Table 3. Reactions of $Ph_2C=C(X)NO_2$ with ethyl phosphites at 150 °C

X[a]	Phosphite[b]	Time(h)	Products[c]
H	$(EtO)_3P$	1	**6a** (73%), **5a** (12%)
H	$(EtO)_3P$	24	**6a** (69%), **5a** (14%)
H	$(EtO)_3P/(EtO)_2P(O)H$ (4:1)	24	**6a** (96%)
H	$(EtO)_3P$	24[d]	**6a** (90%)[e]
H	$(EtO)_3P$/EtOH (1:9)	5 h (95 °C)	**6a** (57%), **2a** (25%), **5a** (5%), **1a** (10%)
PhS	$(EtO)_3P$	0.5	**6b** (99%)[e]
t-BuS	$(EtO)_3P$	1	**6c** (95%)[e]
t-BuS	$(EtO)_2P(O)H$	44	**6c** (25%)[e], 2-(ethylthiyl)-3-phenylindole (16%)[e], $Ph_2CHP(O)(OEt)_2$(10%), $Ph_2CHC(O)SBu$-*t* (6%)[e]
NO_2	$(EtO)_2P(O)H$	0.5	**6a** (52%), **6a** (3%), **1a** (2%), **1d** (12%)
NO_2	$(EtO)_2P(O)H$	3	**6d** (19%)[e], **6a** (6%)[e], $Ph_2CHP(O)(OEt)_2$ (15%)[e]
CH_3	$(EtO)_3P$	1	**6e** (100%)
PhO	$(EtO)_3P$	2	**6f** (89%)[f]

[a]0.3-1 mmol of $Ph_2C=C(X)NO_2$ per mL of phosphite.

Table 3. (Continued)

[b]Volume ratio for mixed solvent.

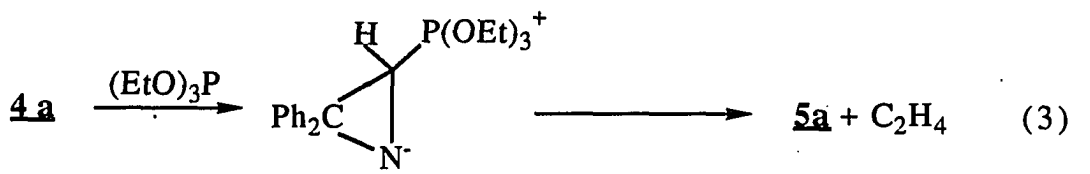
[c]By GC with biphenyl as an internal standard.

[d]30 mol % of MeI added after 18 h.

[e]Isolated yields.

[f]Trace of 1-ethyl-2-phenoxy-3-phenylindole was also separated.

With **1b-1c** or **1e-1f** the yield of the indoles **6b-6c** or **6e-6f** were essentially quantitative in a 1 h reaction at 150 °C. Reaction of **1a** led mainly to the indole **6a** but significant amount of the **5a** were also formed, possibly via reaction 3. We therefore added PH as an acidic



(3)

catalyst in hopes of converting **4a** to **6a** (via Scheme VI). An excellent yield of **6a** (96%) was thus achieved. We also observed that **5a** could be converted to **6a** at 150 °C by refluxing MeI in $(EtO)_3P$ solution. Perhaps alkylation of **5a** at oxygen followed by elimination of HI and $MeOP(OEt)_2$ occurs to regenerate the labile **4a**.

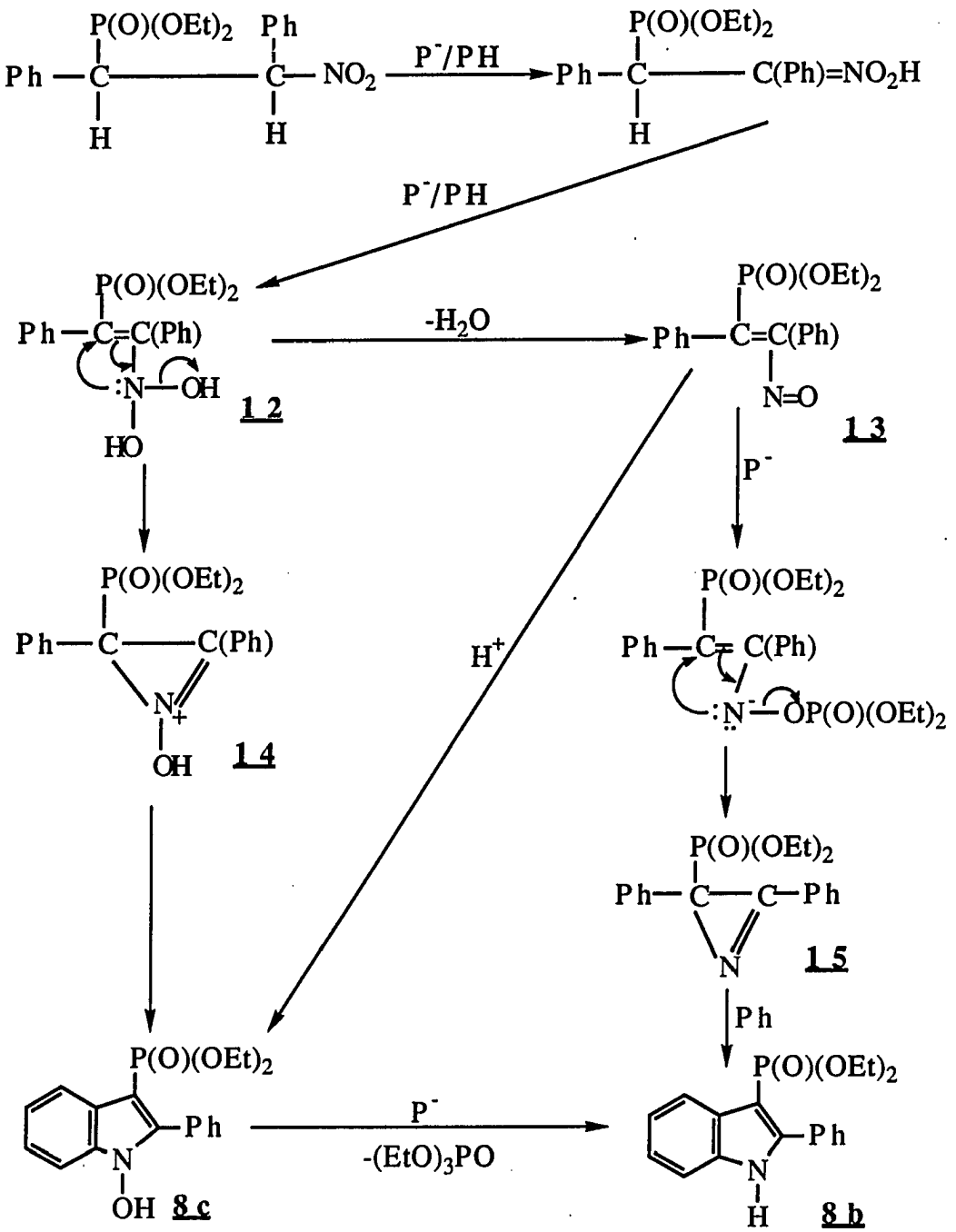
Conversion of (*E*)-PhCH=C(Ph)NO_2 (cis-α-nitrostilbene) into diethyl(1-anilino-2-phenylvinyl)phosphonate, 2-phenyl-3-(diethoxyphosphinyl)indole and 1-hydroxy-2-phenyl-3-(diethoxyphosphinyl)indole

The reaction of 5 equiv of P^- and 5 equiv of PH with (*E*)-PhCH=C(Ph)NO_2 forms diethyl(2-nitro-1,2-diphenylethyl) phosphonate in Me_2SO at 25 °C. In EtOH the P^- generated from 1 equiv of PH and 5 equiv of K_2CO_3, reacted with cis-α-nitrostilbene at 70 °C in 10 h to form **8b** (14%) and **8c** (36%). The formation of these products can be rationalized from further reaction of the initial Michael-type adduct in the presence of P/PH.

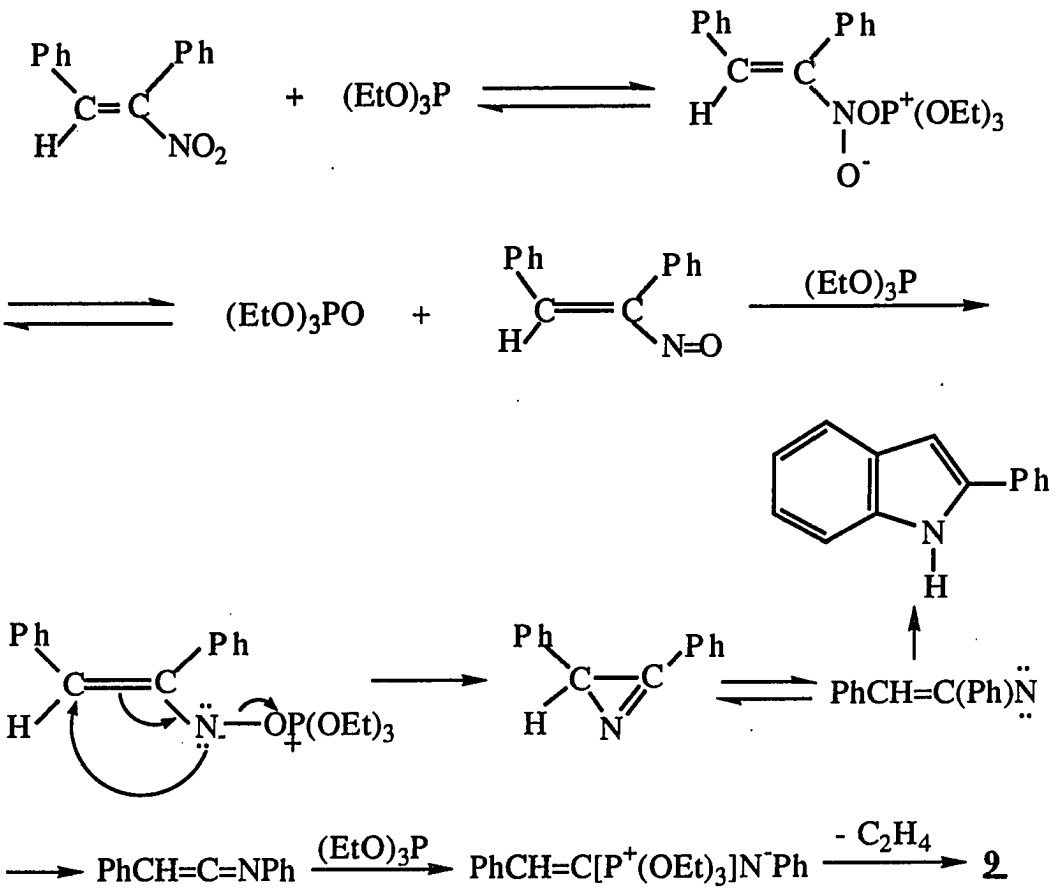
Deprotonation/protonation could lead to **12** and **13** (Scheme VII) and possibly to the azirine **15** and the protonated azirine N-oxide **14**. However, no evidence for the intermediacy of **14** or **15** can be presented. As formulated in Scheme VII, only one equivalent of P^- is required to form the N-hydroxyindole **8c** whereas two equivalents of P^- are required to form the indole **8b**.

Reaction of cis-α-nitrostilbene with $(EtO)_3P$ for 3 h at 150 °C produced compound **9** in 77% yield. A trace of 2-phenylindole was also produced. A possible mechanism for the formation of **9** is given in Scheme VIII. It is not obvious why a ketenimine is formed from PhCH=C(Ph)$\ddot{\ddot{N}}$ and not from Ph_2C=C(X)$\ddot{\ddot{N}}$ with X=H, Ph, CH_3, SPh or *t*-BuS. One possibility is that PhCH=C(Ph)$\ddot{\ddot{N}}$ exists with a trans relationship between the β-phenyl and the nitrogen atom. This effectively prevents the cyclization to give the indole which occurs readily for the nitrenes with two β-phenyl groups.

Scheme VII



Scheme VIII



Compounds **1b-1f** did not yield an isolable aziridine with (EtO)3P at 150 °C. Although P(OEt)3 did not undergo nucleophilic addition to the 3-substituted-2,2-diphenyl-2*H*-azirines **4b-4f**, some of the aziridine **5a** was formed from **1a** under this condition, presumably via 2,2-diphenyl-2*H*-azirine **4a**.

Reaction of ethyl phosphites with β-nitrostyrene

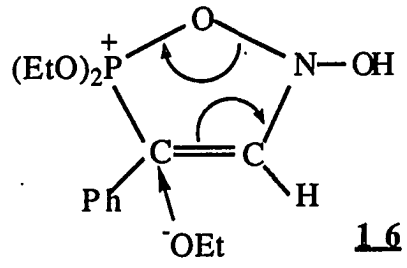
Formation of the 2*H*-azirine from β-nitrostyrene should lead to $PhCH_2CN$ and indole.[4,11] In a previous study of the reaction of $(RO)_3P$ (neat, DME, *t*-BuOH) with $PhCH{=}CHNO_2$ at room temperature, $PhC[P(O)(OR)_2]{=}CH_2$, $PhCH[P(O)(OR)_2]CH_2NO_2$ and $PhC(OR)[P(O)(OR)_2]CH{=}NOH$ were the major products.[12] In view of our success in forming azirine-derived products from α-phenyl-β-nitrostyrenes and cis-α-nitrostilbene, we have examined reactions of $PhCH{=}CHNO_2$ with P^- at 25-35 °C and with $(EtO)_3P$ or $(EtO)_2POH$ at 150 °C. However, indole or $PhCH_2CN$ were not observed.

With 1 equiv of P^- in PH, $PhCH[P(O)(OEt)_2]CH_2NO_2$ was formed slowly at room temperature (10% in 12 h) while with excess P^- the major product was $PhCH[P(O)(OEt)_2]CH_2P(O)(OEt)_2$. Reaction of $PhCH{=}CHNO_2$ for 2 h at 150 °C with 3.2 equiv of $(EtO)_3P$ formed the diphosphonate (15%), $PhC[P(O)(OEt)_2](OEt)CN$ (23%) with traces of $PhC[P(O)(OEt)_2](OEt)CH{=}NOEt$ and $PhC[P(O)(OEt)_2]{=}NOEt$ while reaction with 5 equiv of PH yielded $PhC[P(O)(OEt)_2]{=}CH_2$ (23%), $PhCH[P(O)(OEt)_2]CN$ (52%) and the diphosphonate (7%). With 2.5 equiv P^- in EtOH for 20 h at 60 °C $PhC[P(O)(OEt)_2]{=}CH_2$ (10%) and trace of $PhCH[P(O)(OEt)_2]CH_2[P(O)(OEt)_2]$ was formed.

The formation of $PhC[P(O)(OEt)_2]{=}CH_2$ and the diphosphonate undoubtedly involves the elimination of HNO_2 from $PhCH[P(O)(OEt)_2]CH_2NO_2$. A similar process forming the diphosphonate via $PhCH[P(O)(OEt)_2]{=}CH_2$ from $PhCH{=}CHSO_2Ph$ and P^- in Me_2SO has been recently described.[20] The reaction of $PhCH{=}CHNO_2$

with PH at 150 °C apparently involves the initial formation of $PhCH[P(O)(OEt)_2]CH_2NO_2$ which can undergo either the loss of HNO_2 or deoxygenation-dehydration to form the nitrile.

In $(EtO)_3P$ solution the ethoxy derivatives $PhC[P(O)(OEt)_2](OEt)CN$ and $PhC[P(O)(OEt)_2](OEt)CH=NOEt$ are presumably formed from the previously reported $PhC[P(O)(OEt)_2](OEt)CH=NOH$ whose formation has been suggested to involve the cyclic intermediate **16** derivable from



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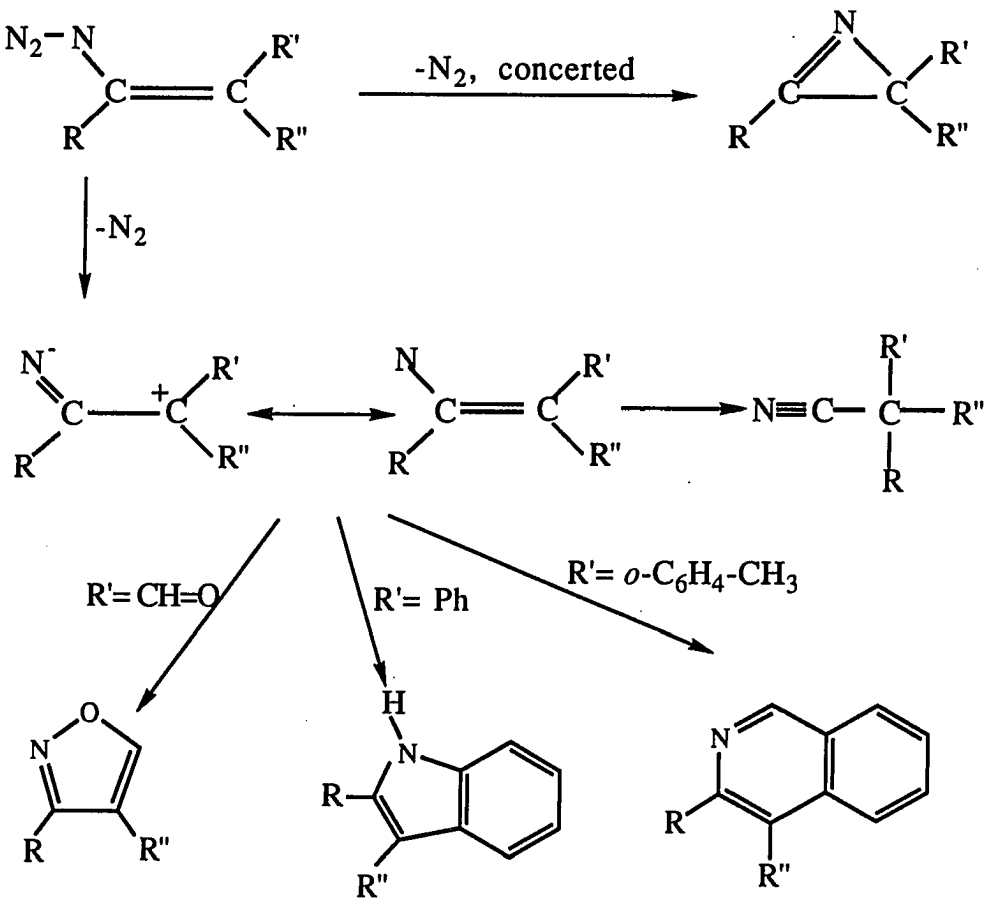
$PhCH[P(OEt)_3^+]CH=NO_2^-$ or $PhCH=CHN(O^-)OP(OEt)_3^+$.[12] The constrasting behaviors of $PhCH=CHNO_2$ or $PhCH=C(Ph)NO_2$ and $Ph_2C=CHNO_2$ with P(III) reagents are a consequence of the presence of the ionizable α-hydrogen atom in the adducts formed from $PhCH=CHNO_2$ or $PhCH=C(Ph)NO_2$.

The formation of azirines in Scheme VI, VII, VIII or the nitrile in Scheme IV have been rationalized without the intervention of a free nitrene. Azirines can also be formed in the photolysis of thermolysis of the terminal vinyl azides.[21] However, even for the vinyl azides the azirine may be formed in a concerted process not

involving the nitrene.[35] A short summary of the formulation by Hassner is given in Scheme IX.[22]

Scheme IX



CONCLUSION

The reactions of RS^- with $Ph_2C{=}C(SPh)NO_2$ to form $Ph_2C{=}CHSR$ have been identified as involving nucleophilic attack upon in the initially-formed Michael-type adducts. The reaction intermediate $Ph_2C{=}CHNO_2$ has been dectected during the reaction. The anion $(EtO)_2PO^-$ can undergo Michael-type addition to $Ph_2C{=}C(SPh)NO_2$ to yield products derived from $Ph_2C[P(O)(OEt)_2]CH(SPh)NO_2$ such as $Ph_2C[P(O)(OEt)_2]CH_2NO_2$, $Ph_2C[P(O)(OEt)_2]CHO$ and $Ph_2C[P(O)(OEt)_2]CN$. Deoxygenation of $Ph_2C{=}C(Y)NO_2$ by $(EtO)_2PO^-$ in Me_2SO at room temperature also yields azirines which can be isolated in the case of Y=*t*-BuS or trapped by addition of $(EtO)_2PO^-$ to yield an aziridine in the case of Y=H or CH_3. At 150 °C $(EtO)_3P$ reacts with $Ph_2C{=}C(Y)NO_2$ (Y=H, CH_3, NO_2, OPh, PhS, SBu-*t*) to form the corresponding indoles by the deoxygenation of the nitro group to yield azirine which subsequently forms the indole via the nitrene intermediate.

EXPERIMENTAL SECTION

General methods

^{1}H and ^{13}C NMR spectra were obtained with Nicolet NT300 or Varian Unity 500 spectrometers with tetramethylsilane as the internal standard. ^{31}P NMR spcetra were obtained with a Brucker WM-200 spectrometer and reported in ppm relative to external 85% phosphoric acid. Mass spectra were obtained in the GC mode (EI or CI) or with a solids inlet probe (CI) by a Finnigan 4000 (INCOS data system). High resolution spectra were obtained by a Kratos MS-50 spectrometer. Infrared spectra were obtained in the FT mode by an IBM IR 99 spectrometer. Neat spectra were recorded between NaCl plates. Elemental analyses were performed by Galbraith Laboratories, Inc. All mp's were determined on a Thomas-Hoover capillary melting point appartus and are uncorrected. Most products were isolated by flash column chromatography on silica gel (230-400 mesh ASTM). Analytical gas chromatography was performed with a Varian 3700 chromatograph with a Hewlett Packard 3390A integrator employing biphenyl as the internal standard and 7% OV-3 as the stationary phase. The purity of all title compounds was judged to be > 95% since significant impurities could not be detected by GC or by ^{1}H NMR.

Material

Dimethyl sulfoxide was vacuum distilled and stored over molecular sieves or CaH_2. The $(EtO)_3P$, $(EtO)_2P(O)H$, PhSH, *t*-BuSH,

$PhCH=CHNO_2$, *t*-BuOK and $Ph_2C=CH_2$ used were obtained from Aldrich Chem. Co. The anions PhS^-, *t*-BuS^-, $(EtO)_2PO^-$ were prepared in situ by reaction of 1 equiv of *t*-BuOK with the conjugate acids under N_2.

Reactants prepared according to literature procedures were **1a**,[23] **1b**,[1] **1c**,[1] **1d**,[24] **1e**,[23] **1f**,[1] **2d**[1] and (*E*)$PhCH=C(Ph)NO_2$.[23] The following reaction products were either prepared according to literature procedures or had physical and spectroscopic properties in agreement with literature values: $Ph_2C=C(SPh)_2$,[25] $Ph_2CH[P(O)(OEt)_2]$,[26] $PhSP(O)(OEt)_2$,[27] $PhCH[P(O)(OEt)_2]CH_2NO_2$,[12] $PhC[P(O)(OEt)_2]=CH_2$,[12,20] $PhC[P(O)(OEt)_2]CH_2P(O)(OEt)_2$,[20] 3-phenylindole,[28] 1,1-diphenyl-2,2-bis(phenylthiyl)ethylene,[29] 2-methyl-3-phenylindole.[13]

Potassium salt of diethyl (2,2-dinitro-1,1-diphenylethyl)-phosphonate (**2d**)

1,1-Dinitro-2,2-diphenylethylene (5 mmol) in THF (20 mL) was added dropwise to a mixture of $(EtO)_2P(O)H$ (5.5 mmol) and *t*-BuOK (5.5 mmol) in 30 mL of THF at 35-40 °C. The solution turned from a deep brown to yellow. After stirring for 2 h, the THF was evaporated to give a yellow solid which was recrystallized from ethanol to give a 49% yield of $C_{18}H_{20}N_2O_7PK$ (elemental Anal. C, H, N), mp 133-135 °C; ^1H NMR (Me_2SO-*d* 6) δ 7.20-7.06(m, 10H), 3.76-3.66(m, 2H), 3.45-3.33(m, 2H), 0.79(t, *J*=7.2 Hz, 6H). The potassium salt (5 mmol) in 50 mL of EtOH was titrated with alcoholic HCl until the yellow solution became colorless. Upon cooling to 0 °C a 60% yield of **2d**, mp 131-133

°C (lit.[1] 128-129 °C) was obtained; ^{1}H NMR ($CDCl_3$) δ 7.68(d, J_{PH}=9.6 Hz, 1H), 7.49-7.30(m, 10H), 4.07-3.96(m, 4H), 1.15(td, J=7.5, 0.6 Hz, 6H); GCMS (CI, isobutane), m/z (relative intensity) 409 ($M+1^+$, 100), 364(28), 346(10), 319(9), 305(3), 250(3), 226(2), 167(5), 165(1), 139(9).

Diethyl(2-nitro-1,1-diphenylethyl)phosphonate (**2a**)

Solid $Ph_2C{=}CHNO_2$ (0.49 mmol) was added to a mixture of $(EtO)_2P(O)H$ (1 mL=7.7 mmol) and *t*-BuOK (0.49 mmol). After stirring for 1 h the solution was poured into 5 mL of brine and extracted twice with 5 mL of CH_2Cl_2. The extract was washed, dried, filtered and concentrated to give an oil which was purified by flash column chromatography with hexane (75%) - ethyl acetate (25%) to give 37% of **2a**, mp 74-75 °C; ^{1}H NMR ($CDCl_3$) 7.55-7.32(m, 10H), 5.46(d, J_{PH}=9.0 Hz, 2H), 3.94-3.84(m, 2H), 3.78-3.68(m, 2H), 1.16(t, J=7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 136.1(d, J_{PC}=7.2 Hz), 129.7(J_{PC}=1.6 Hz), 127.9, 127.7, 78.7, 63.9(d, J_{PC}=7.0 Hz), 55.6(d, $^1J_{PC}$=132 Hz), 16.1(d, J_{PC}=5.0 Hz). GC and HRMS, m/z (relative intensity) 363.1246(M^+, 2, calcd for $C_{18}H_{22}NO_5P$ 363.1236), 317.1304(M^+-NO_2, 27, calcd for $C_{18}H_{20}O_3P$ 317.1302), 261(8), 226(14), 180(100), 165(26), 109(28), 77(6).

1,1-Diphenyl-2-(phenylthiyl)ethylene from 1-nitro-2,2-diphenylethylene (**1a**)

The nitroalkene (0.94 mmol) in 10 mL of Me_2SO was added dropwise to a solution of 4.75 mmol each of PhSH and *t*-BuOK in 10

mL of Me_2SO. After stirring for 30 h under N_2 the solution was hydrolyzed with 20 mL of brine and extracted three times with 20 mL of ether. The ether extract was washed, dried and concentrated to give an oil that was purified by flash column chromatography (hexane) to give a 94% isolated yield of $Ph_2C{=}CHSPh$ whose spectra and GC retention time agreed with an indpendently prepared sample.[25]

Reaction of PhSK with 1-nitro-2,2-diphenyl-1-(phenylthiyl)ethylene (**1b**)

Reaction of **1b** (1 mmol) with 5 mmol each of PhSH and *t*-BuOK in 50 mL of Me_2SO containing biphenyl (1mmol) as an internal standard was followed by GC after hydrolysis with brine and ether extraction (Fig. 1). After 72 h there was an 87% yield of $Ph_2C{=}CHSPh$, 0.3% of $Ph_2C{=}CHNO_2$ and a 1.3 mmol of PhSSPh. In Me_2SO which had not been thoroughly dried, appreciable quantities of $Ph_2C{=}O$ were also formed.

On one occasion a product was isolated after column and thin layer chromatography which GCMS did not indicate to be present in the original extract from the 1 h reaction. This material was unstable but gave a GCMS suggestive of **3a**, m/z (relative intensity) 336(9), 335(18), 334(M^+-PhS, 75), 225(M^+-Ph_2S_2, 100), 210(94), 192(27), 178(52), 165(48), 121(38), 109(2), 91(41), 77(10). A similar MS was initially observed in a MS solids inlet probe but with time the MS changed to give the spectrum of $Ph_2C{=}C(SPh)_2$, m/z (relative

intensity) 398(2), 397(4), 396(M^+, 13), 287(36), 254(16), 231(100), 153(33), 121(90).

2-(*tert*-Butylthiyl)-1,1-diphenylethylene

Solid **1b** (0.5 mmol) was added to 2.5 mmol of *t*-BuSK in 20 mL of Me_2SO and stirred for 23 h under N_2. The product was hydrolyzed with brine, extracted by CH_2Cl_2 and the filtrate dried over Na_2SO_4. Using toluene as an internal standard the ^1H NMR yield of $Ph_2C{=}CHSBu$-*t* was 88%. Material isolated by column chromatography with hexane had mp 56-58 °C; ^1H NMR ($CDCl_3$) δ 7.40-7.18(m, 10H), 6.77(s, 1H), 1.43(s, 9H); GC and HRMS, m/z (relative intensity) 270(2.7), 268.12846(M^+, 42, calcd for $C_{18}H_{20}S$ 268.12858), 212(100), 178(20), 165(12), 77(6), 57(28).

α-(Diethoxyphosphinyl)diphenylacetaldehyde

Solid **1b** (1 mmol) was added to a mixture of $(EtO)_2P(O)H$ (3mL) and *t*-BuOK (2 mmol). The green solution was stirred for 2 min, poured into 10 mL of brine and extracted twice with 10 mL of CH_2Cl_2. The extract was washed, dried, filtered and concentrated to give an oil which was purified by flash column chromatography using hexane (95%) - ethyl acetate (5%) to give a 50% yield of the aldehyde mp 127-132 °C; ^1H NMR ($CDCl_3$) δ 9.93(d, J_{PH}= 3.0 Hz), 7.60-7.20(m, 10H), 4.12-3.87(m, 4H), 1.21(t, J=6.9 Hz, 6H); FTIR(neat) at 1730 cm^{-1}; GC and HRMS, m/z (relative intensity) 332.1170(M^+, 0.5, calcd for $C_{18}H_{21}O_4P$ 332.1174), 304(40), 276(7), 248(19), 207(10), 178(19),

165(100), 105(70), 77(11); GCMS (CI, methane) m/z (relative intensity) 333(MH^+, 100), 305(20), 304(13), 287(1), 183(3), 165(1), 121(2), 111(2), 105(1).

α-(Diethoxyphosphinyl)diphenylacetonitrile (7d)

Addition of 2d (0.217 mmol) to $(EtO)_3P$ (1 mL, 5.8 mmol), followed by heating at 150 °C for 1h gave after vacuum distillation of the unreacted $(EtO)_3P$ and $(EtO)_3PO$ which had been formed, an oily residue of 7d (>95% yield by GC). Pure 7d was obtained by TLC using hexane (90%) - ethyl acetate (10%) to give material with mp 83-84 °C (from hexane); ^1H NMR ($CDCl_3$) δ 7.68-7.25(m, 10H), 4.01-3.95(m, 2H), 3.92-3.78(m, 2H), 1.14(t, J=7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 134.2(d, J_{PC}=4.4 Hz), 128.8, 128.6, 128.5, 118.8(d, J_{PC}=12.6 Hz), 65.1(d, J_{PC}=7.1 Hz), 52.9(d, $^1J_{PC}$=137 Hz), 16.2(d, J_{PC}=4.1 Hz); FTIR at 2250 cm^{-1}; GC and HRMS, m/z (relative intensity) 329.1179(M^+, 70, calcd for $C_{18}H_{20}NO_3P$, 329.1181), 304(4), 273(6), 193(100), 165(69), 109(59), 91(3), 77(4).

Reaction of 0.27 mmol of 2a with 1 mL of $(EtO)_3P$ at 150 °C for 1 h gave by GC 7d (23%), $Ph_2CHP(O)(OEt)_2$ (26%) and 5a (7%). With a 1:1 mixture of $(EtO)_3P$ (2.9 mmol) and $(EtO)_2P(O)H$ (3.9 mmol) for 1 h at 150 °C, the GC yield of 7d was 22% and $Ph_2CHP(O)(OEt)_2$ (8%) while a 13 h reaction period gave only 14% of 7d and 19% of $Ph_2CHP(O)(OEt)_2$. Reaction of 2d (0.19 mmol) with $(EtO)_2P(O)H$ (1mL) at 150 °C for 1 h gave low yield of 7d (14%) and $Ph_2CHP(O)(OEt)_2$ (3%).

3-(Diethoxyphosphinyl)-2,2-diphenylaziridine (**5a**)

Compound **2a** (0.14 mmol) was added to 1 mL of $(EtO)_2P(O)H$ and 0.14 mmol of *t*-BuOK. After stirring 5 h at room temperature, the solution was poured into 5 mL of brine and extracted twice with 5 mL of CH_2Cl_2. The extract was washed, dried, filtered and concentrated to give by GC 90% of **5a**. The material was chromatographed with hexane (90%) - ethyl acetate (10%) but remained upon the column from which it was eluted with ethyl acetate to give an oil having FTIR (neat) at 3238 cm^{-1}(NH); ^1H NMR ($CDCl_3$) δ 7.60-7.20(m, 10H), 4.00(p, J=7.2 Hz, 2H), 3.85-3.70(m, 1H), 3.60-3.40(m, 1H), 2.70(d, J=16.5 Hz, 1H), 2.00(br, s), 1.24(t, J=7.2 Hz, 3H), 1.05(t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 143.6(d, J_{PC}=0.9 Hz), 138.4(d, J_{PC}=2.0 Hz), 132.2, 129.9, 128.8, 128.3, 128.1, 127.9, 127.5, 127.3, 126.9, 126.8, 62.0(d, J_{POC}=7.1 Hz), 61.9(d, J_{POC}=6.0 Hz), 49.4(d, J_{PC}=2.6 Hz), 38.5(d, $^1J_{PC}$=199 Hz), 16.1(d, J_{PC}=6.6 Hz), 16.0(d, J_{PC}=6.0 Hz). The assignment of J_{PC} and δ for the diastereotopic carbons of the ethoxy groups was established by comparison of the 75 and 125 MHz proton-decoupled ^{13}C spectra. In **5a** there is restricted rotation of the phenyl groups and 12 different aromatic carbon atoms are observed. The ethoxy groups in **5a** are diastereotopic as are the individual methylene hydrogen atoms. A 2D COSY spectrum showed that the δ 1.05 methyl is coupled to the methylene hydrogens at δ 3.78 and 3.50 while the methyl at δ 1.24 is coupled to the methylene group at δ 4.0 (the methylene hydrogens are also coupled to P with $^3J_{PH}$ 7.2 Hz). The methine hydrogen at δ 2.70 is not coupled to any other hydrogen atom

therefore is coupled to phosphorous, $^2J_{PH}$=16.5 Hz (coupling to the methine ^{13}C is 164 Hz). The ^{31}P NMR spectrum is at δ 20.94 (d of pentets, J_{PH}=16.8 Hz). The GCMS and direct inlet HRMS spectra showed significant differences; GCMS (EI), m/z (relative intensity) 331(0.5), 330(1), 275(1), 207(1), 247(1), 221(1), 208(7), 194(34), 165(9), 91(100), 77(4); GCMS (CI, isobutane), m/z (relative intensity) 332(MH^+, 100), 208(1), 194(3), 165(0.4); HRMS 331.13304(M^+, 6, calcd for $C_{18}H_{22}NO_3P$ 331.13374), 330.1254(M-1^+, 6; calcd for $C_{18}H_{21}NO_3P$ 330.12591), 304(11), 274(4), 248(3), 195(9), 194(37), 193(100), 178(4), 167(10), 166(18), 165(39), 91.05467(8, calcd for $C_7H_7^+$ 91.05478).

Reaction of **1b** with $(EtO)_2PO^-$

With excess P^- (10 equiv.) in dry Me_2SO the reaction leads mainly to $PhSP(O)(OEt)_2$, **2a**, **5a** and **7d**. The products listed in Table 1 were observed after workup with brine, extraction by CH_2Cl_2 and analysis by GC and GCMS. At lower P^-/**1a** ratios or in the presence of $(EtO)_2P(O)H$, the yield of the indole **6a** increased. In moist Me_2SO, Ph_2C=O (and products derived from Ph_2C=O) are formed from the hydrolysis of **1b**. In one experiment with 2 equiv of P^- in moist Me_2SO the ethyl ester of α-aminodiphenylacetic acid [$Ph_2C(NH_2)CO_2Et$] was isolated by column chromatography; ^1H NMR (Me_2SO-*d* 6) δ 7.5-7.2(m), 4.0(q, *J*=7.2 Hz, 2H), 1.157(t, *J*=7.2 Hz, 3H), 1.185(s, 2H); FTIR (neat) at 3287, 1711, 1688 cm^{-1}; HRMS, m/z (relative intensity) 255.12565(M^+, 73, calcd for $C_{16}H_{17}NO_2$

255.12593), 226.0868($C_{14}H_{12}NO^+$, 97), 182.0968($C_{13}H_{12}N^+$, 100), 180.0815($C_{13}H_{10}N^+$, 20), 178.0863($C_{10}H_{12}NO_2^+$, 12), 167.0857($C_{13}H_{11}^+$, 37), 165.0707($C_{13}H_9^+$, 36), 152.0628($C_{12}H_8^+$, 13), 106.0657($C_7H_8N^+$, 10), 104.0501($C_7H_6N^+$, 62). All fragments were within 1.5 ppm of the assigned atomic composition.

Reaction of **2d** with $(EtO)_2PO^-$

The solid potassium salt of **2d** (0.27 mmol) was added to $(EtO)_2P(O)H$ (1 mL) containing *t*-BuOK (1.35 mmol). Workup after stirring for 30 min showed the presence of **7d**, $Ph_2CHP(O)(OEt)_2$ and an intermediate with a GCMS, m/z (relative intensity) 345(3), 317(1), 284(1), 292(1), 208(100), 165(8), 105(2), 77(17). After stirring for 26 h before workup, the above reaction mixture did not show the intermediate of m/z 345 by GCMS and gave by GC 15% of **7d** and 20% of $Ph_2CHP(O)(OEt)_2$.

3-(*tert*-Butylthiyl)-2,2-diphenyl-2*H*-azirine (**4c**)

The nitroalkene **1c** (1.2 mmol) in 25 mL of Me_2SO was added dropwise to a mixture of $(EtO)_2P(O)H$ (12 mmol) and *t*-BuOK (12 mmol) in 25 mL of Me_2SO and the resulting solution stirred for 2 h before hydrolysis with 50 mL of brine. The product was extracted with two portions of 50 mL of CH_2Cl_2 and the extract washed, dried over Na_2SO_4 and concentrated to an oily residue. Flash column chromatograpohy using hexane (99%) - ethyl acetate (1%) gave a product which was seperated by TLC into **4c** (49%) and 9% of a

hydrolysis product. The azirine 4c had mp 69-72 °C; ^{1}H NMR ($CDCl_3$) δ 7.70-7.20(m, 10H), 1.67(s, 9H); FTIR (CH_2Cl_2) at 1654 cm^{-1}; GC and HRMS m/z (relative intensity) 283(M^+, 0.2), 281.12349(M^+, 3, calcd for $C_{18}H_{19}NS$ 281.122383), 225(6), 193(20), 192(100), 177(28), 165(45), 77(4), 57(21).

The isolated hydrolysis product mp 101-102.5 °C, was not detected by GCMS before column chromatography. The product in CCl_4 had FTIR absorption at 3207(s, NH), 3000(br, OH), 1583(s, C=N) cm^{-1}. The ^{1}H NMR ($CDCl_3$) contained a broad singlet at δ 9.63 with other absorption at δ 7.50-7.30(m, 11H) and 1.49(s, 9H); HRMS, m/z (relative intensity) 299.1350 (calcd for $C_{18}H_{21}NOS$ 299.1344); GCMS (CI, methane) m/z (relative intensity) 300(MH^+, 10), 284(4), 254(18), 244(17), 227(16), 226(100), 184(24), 183(59), 166(8), 105(10). The MS data seems to favor the thioimidate stucture, $Ph_2C(OH)C(SBu\text{-}t)=NH$, rather than the oxime $Ph_2C(SBu\text{-}t)CH=NOH$. The HRMS is dominated by m/z 184.0881 (70%), 183.0810(89%) and 105.0342(100%). These fragments are within 2 ppm of the calculated masses for $C_{13}H_{12}O^+$($Ph_2CHO^{\cdot+}$), $C_{13}H_{11}O^+$(Ph_2CHO^+) and $C_7H_5O^+$($PhCO^+$), respectively and no fragments containing sulfur and/or nitrogen come close to the observed values of m/z (e.g. $PhCH=NH^{\cdot+}$ is 160 ppm lower than the mass measured for the 105 peak). The structure thus requires the unit Ph_2CO as in $Ph_2C(OH)C(SBu\text{-}t)=NH$. Finally, the product can be easily rationalized by attack of H_2O upon $Ph_2C=C(SBu\text{-}t)NH^+$ derived by protonation of the azirine 4c.

α-(*tert*-Butylthiyl)diphenylacetonitrile (7c)

Reaction of **1c** with P^- in $(EtO)_2P(O)H$ produced mainly the indole **6c**. Column chromatography after a 24 h reaction period also yields the nitrile **7c**, mp 78-79 °C, which gives an FTIR spectrum without C=N absorption at ~1650 cm^{-1} and with a C≡N absorption at 2233 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30-7.16(m, 10H), 1.59(s, 9H); the MS was identical to that observed for **4c**.

3-Phenylindole (6a)

Material synthesized according to the literature but using $ZnCl_2$ as the catalyst, had mp 85-86 °C(lit.[28] 86-87 °C); ^1H NMR ($CDCl_3$) δ 8.24(br s, 1H, NH), 8.10-7.10(m, 10H); ^{13}C NMR ($CDCl_3$) 133.6, 135.5, 128.7, 127.4, 125.9, 125.7, 122.4, 121.7, 120.3, 129.8, 118.3, 111.4; FTIR (CCl_4) at 3412 cm^{-1}; GC and HRMS, m/z (relative intensity) 194(15), 193.08917(M^+, 100, calcd for $C_{14}H_{11}N$ 193.08915), 177(1), 165(30), 115(2), 97(11), 82(14), 77(2).

3-Phenyl-2-(phenylthiyl)indole (6b)

Compound **1b** (0.33 mmol) in 1 mL of $(EtO)_3P$ at 150 °C for 30 min followed by vacuum distillation of the volatiles gave a red oil as a residue which upon flash column chromatography with hexane (95%) - ethyl acetate (5%) gave a 99% yield of the indole, mp 199-203 °C; ^1H NMR ($CDCl_3$) δ 8.16(br s, 1H), 7.80-7.0(m, 14H); ^{13}C NMR ($CDCl_3$) δ 138.9, 138.8, 133.7, 129.6, 129.1, 128.3, 127.1, 127.0, 126.8, 125.9, 124.4, 123.9, 121.7, 120.5, 111.0; FTIR (neat) at 3402 cm^{-1}; GC and

HRMS, m/z (relative intensity) 301.0930(M^+, 100, cacld for $C_{20}H_{15}NS$, 301.0925), 267(10), 233(26), 165(7), 151(4), 134(5), 77(5).

2-(*tert*-Butylthiyl)-3-phenylindole (**6c**)

Reaction of **1c** (0.56 mmol) in 1 mL of $(EtO)_3P$ at 150 °C for 30 min gave a 95% isolated yield of the indole after flash column purification; mp 137-139 °C; ^1H NMR ($CDCl_3$) δ 8.16(br s, <1H), 7.82-7.10(m, 9H), 1.13(s, 9H); ^{13}C NMR ($CDCl_3$) δ 136.1, 134.7, 130.4, 128.0, 127.4, 126.3, 124.9, 124.0, 123.3, 120.1, 120.0, 110.9, 49.5, 31.1; FTIR (CCl4) at 3412 cm^{-1}; GC and HRMS, m/z (relative intensity) 283(0.7), 281.1233(M^+, 11, calcd for $C_{18}H_{19}NS$ 281.1238), 225(100), 193(7), 180(1), 165(6), 77(2), 57(14). Freshly prepared material does not contain a C=N FTIR absoption. However, absorption develops with time at 1620 cm^{-1} suggesting the formation of the 3H-indole.

2-(Ethylthiyl)-3-phenylindole form the reaction of **1c** with $(EtO)_2P(O)H$

Material isolated by column chromatography had mp 133-135 °C; FTIR (CCl_4) at 3406, 1603 cm^{-1}; ^1H NMR 8.11(br s, <1H), 7.70-7.69(m, 9H), 2.66(q, *J*=7.2 Hz, 1.6H), 2.83(q, *J*=7.2 Hz, 0.4H), 1.09(t, *J*=7.2 Hz, 2.4H), 1.04(t, *J*=7.2 Hz 0.6H). The NMR spectrum is consistent with a mixture of 4.3 parts of the indole to 1 part of the 3H-indole. The mixture has a GCMS m/z (relative intensity) 255(6), 253(100), 234(96), 193(3), 178(2), 165(7), 77(3); GCMS (CI, isobutane) m/z

(relative intensity) 310($M+57^+$, 5), 254($M+1^+$, 100); HRMS 253.09222 (cacld for $C_{16}H_{15}NS$ 253.09253).

S-*tert*-Butyl diphenylthioacetate

Material isolated by column chromatography from the reactions of **1c** with $(EtO)_2P(O)H$ at 150 °C had ^1H NMR ($CDCl_3$) δ 7.32-7.25(m, 10H), 5.10(s, 1H), 1.45(s, 9H); FTIR (neat) at 1686 cm^{-1}; HRMS m/z 284.1231 (calcd for $C_{18}H_{20}OS$ 284.1235); GCMS (CI, isobutane) m/z (relative intensity) 258($M+1^+$, 58, 271(6), 229(64), 209(9), 167(100), 152(5), 123(6).

O-Ethyl diphenylacetimidate ($Ph_2CHC(OEt)=NH$)

Material isolated by column chromatography from the reaction of **1c** with $(EtO)_2P(O)H$ at 150 °C had ^1H NMR ($CDCl_3$) δ 7.40-7.20(m, 10H), 5.65(br s, 1H), 4.90(s, 1H), 3.30(m, 2H), 1.09(t, J= 7.2 Hz, 3H); FTIR (neat) at 3288, 1639 cm^{-1}; HRMS m/z (relative intensity) 239.13061(M^+, 1, calcd for $C_{16}H_{17}NO$ 239.13102), 168.0936($C_{13}H_{12}^+$, 100), 167.0861($C_{13}H_{11}^+$, 75), 165.0709($C_{13}H_9^+$, 42), 152.0627($C_{12}H_8^+$, 20).

2-Nitro-3-phenylindole (**6d**)

Reaction of 8 mmol of **1d** in 8 mL of $(EtO)_2P(O)H$ for 25 min at 150 °C gives by GC a 52% yield of **6d**. A 33% yield of **6d**, mp 157-159 °C (from hexane) was isolated after vacuum distillation of the volatiles and flash column purification of the residue using hexane (99%) -

ethyl acetate (1%); FTIR (CCl_4) at 3237 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.29(1H), 7.70-7.20(9H); ^{13}C NMR ($CDCl_3$) δ 133.4, 139.4, 139.2, 127.5, 127.3, 127.2, 125.6, 122.8, 122.3, 118.5, 112.0; GC and HRMS, m/z (relative intensity) 238.07461(M^+, 100, calcd for $C_{14}H_{10}N_2O_2$ 238.07423), 221(5), 208(16), 190(41), 180(15), 165(36), 152(11), 77(19).

Diethyl S-phenyl and S-*tert*-butylthiophosphate

The S-phenyl thiophosphate prepared from the reaction of $(EtO)_3P$ with Ph_2S_2 by a literature procedure[27] has ^1H NMR ($CDCl_3$) δ 7.62-7.26(m, 5H), 4.27-4.10(m, 4H), 1.31(t, *J*=6.9 Hz, 6H); HRMS, m/z 246.0484 (calcd for $C_{10}H_{15}O_3PS$ 256.0480). The S-*tert*-butyl ester was identfied by GCMS only, m/z (relative intensity) 226(M^+, 1), 170(100), 142(30), 126(48), 114(43), 92(23), 57(60).

α-(Diethoxyphosphinyl)phenylacetonitrile

Reaction of 5 mmol of $PhCH{=}CHNO_2$ in 3 mL of $(EtO)_2P(O)H$ at 150 °C for 2 h gave an isolated yield of $PhCH[P(O)(OEt)_2]CN$ of 52% as a liquid after vacuum distillation of the volatiles and chromatography with hexane (90%) - ethyl acetate (10%). Also isolated were $PhCH[P(O)(OEt)_2]{=}CH_2$ (23%) and $PhCH[P(O)(OEt)_2]{=}CH_2NO_2$ (9%). The cyanophosphonate had FTIR (neat) at 2247 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45-7.20(m, 5H), 4.20(d, *J*= 26.4 Hz, 1H), 4.14-3.90(m, 1H), 1.24(t, *J*=7.5 Hz, 3H), 1.18(t, *J*=7.5 Hz, 3H); GC and HRMS, m/z (relative intensity) 253.08721(M^+, 41, calcd for $C_{12}H_{16}NO_3P$ 253.08679),

225(4), 197(3), 137(16), 117(90), 109(100), 89(24), 81(40), 77(3); GCMS (CI, ammonia) m/z (relative intensity) 271($M+18^+$, 100), 254($M+1^+$, 6).

α-Ethoxy-α-(diethoxyphosphinyl)phenylacetonitrile

Reaction of 10 mmol of $PhCH=CHNO_2$ with 5 mL of $(EtO)_3P$ for 2 h at 150 °C followed by distillation of the volatiles and column chromatography with hexane (80%) - ethyl acetate (20%) gave the ethoxynitrile in 23% yield as a liquid. Also isolated were traces of $PhC[P(O)(OEt)_2]=NOEt$ and $PhC(OEt)[P(O)(OEt)_2]CH=NOEt$. A 15% yield of $PhC[P(O)(OEt)_2]=CH_2P(O)(OEt)_2$ was eluted from the column with pure ethyl acetate. $PhC(OEt)[P(O)(OEt)_2]CN$ has FTIR (neat) at 2235 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70-7.40(m, 5H), 4.29(p, *J*=7.2 Hz, 2H), 4.13-3.99(m, 1H), 3.97-3.82(m, 1H), 3.77-3.60(m, 1H), 3.54-3.40(m, 1H), 1.37(dd, *J*=5.9, 7.5 Hz, 3H), 1.28(t, *J*=7.2 Hz, 3H), 1.16(td, *J*=7.2, 0.6 Hz, 3H); GC and HRMS, m/z (relative intensity) 297.11341(M^+, 7, calcd for $C_{14}H_{20}NO_4P$ 297.11300), 252(1), 213(1), 160(13), 132(20), 105(100), 77(11).

Ethyl imino ethers of α-ethoxy-α-(diethoxyphosphinyl)-phenylacetaldehyde oxime and of diethyl α-(hydroxyimino)benzylphosphonate

Traces of the imino ethers were isolated from the above reaction by column chromatography. $PhC(OEt)[P(O)(OEt)_2]C=NOEt$ isolated as a liquid had ^1H NMR ($CDCl_3$) δ 7.71(d, *J*=11.1 Hz, 1H), 7.65-7.28(m, 5H), 4.21(q, *J*= 7.2 Hz, 2H), 4.15-3.99(m, 4H), 3.80-3.68(m, 1H), 3.58-

3.46(m, 1H), 1.33-1.20(m, 12H); GC and HRMS, m/z (relative intensity), 343.1549(M^+, 1, calcd for $C_{16}H_{26}NO_5P$ 343.1549), 314(1), 298(2), 270(1), 241(1), 207(13), 206(100), 178(28), 105(30), 100(19), 77(16).

The PhC[P(O)(OEt)2]=NOEt isolated as a liquid had FTIR (neat) at 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.92-7.30(m, 5H), 4.88(q, *J*=7.2 Hz, 2H), 4.09(p, *J*=7.2 Hz, 4H), 1.40(t, *J*=7.2 Hz, 3H), 1.18(t, *J*=7.2 Hz, 6H); GC and HRMS, m/z (relative intensity) 285.11244(M^+, 13, calcd for $C_{13}H_{20}NO_4P$ 285.11300), 284(21), 267(8), 240(8), 197(7), 168(11), 152(13), 138(49), 105(31), 104(100), 91(18), 77(33); GCMS (CI, ammonia), m/z (relative intensity) 303($M+18^+$, 29), 286($M+1^+$, 100).

2-Phenoxy-3-phenylindole (6f)

Reaction of 0.48 mmol of **1f** in 2 mL of $(EtO)_3P$ at 150 °C for 2 h followed by vacuum distillation of the volatiles gave a red oil as a residue which upon flash column chromatography with hexane (95%), - ethyl acetate (15%) gave the indole (NMR with toluene as an internal standard gave a yield of 89%), mp 112-114 °C; ^1H NMR ($CDCl_3$) δ 7.86-6.94(m, 14H), 7.72(br s, 1H); ^{13}C NMR ($CDCl_3$) δ 157.3, 142.7, 133.0, 130.9, 129.7, 128.5, 128.1, 126.1, 125.8, 123.3, 121.9, 120.6, 119.3, 116.3, 110.8, 102.4; FTIR (neat) at 3396 cm^{-1}; GC and HRMS, m/z (relative intensity) 286(22), 285.11525(M^+, 100, calcd for $C_{20}H_{15}NO$ 285.11536), 208(90), 180(37), 152(31), 77(53).

1-Ethyl-2-phenoxy-3-phenylindole

A trace of this product was isolated from the above reaction by column chromatography. The isolated product had ^{1}H NMR ($CDCl_3$) δ 7.91-6.91(m, 14H), 4.04(q, *J*=7.2 Hz, 2H), 1.28(t, *J*=7.2 Hz, 3H); GC and HRMS, m/z (relative intensity) 314(28), 313.14585(M^+, 100, calcd for $C_{22}H_{19}NO$ 313.14667), 236(56), 207(16), 193(24), 180(18), 165(33), 152(18), 77(41).

2-Methyl-3-phenylindole (**6e**)[13]

Reaction of 0.3 mmol of **1e** in 1mL of $(EtO)_3P$ at 150 °C for 1 h followed by vacuum distillation of the volatiles gave 100% of **6e** by ^{1}H NMR with toluene as an internal standard. Flash column separation with hexane (97%) - ethyl acetate (3%) gave a pure colorless solid, mp 57-59 °C (lit.[13] 58-60 °C); FTIR (neat) at 3406 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 7.72(br s, 1H, NH), 7.67-7.07(m, 9H), 2.40(s, 3H); ^{13}C NMR ($CDCl_3$) δ 135.4, 135.2, 131.4, 129.4, 128.5, 127.8,125.8, 121.5, 120.0, 118.7, 114.4, 110.3, 12.4; GCMS, m/z (relative intensity) 208($M+1^+$, 15), 207(M^+, 100), 191(2), 178(9), 165(7), 103(17), 77(5).

3-Methyl-3-(diethoxyphosphinyl)-2,2-diphenylaziridine (**5b**)

Compound **1e** (0.83 mmol) was added to P^- (5 equiv) and PH (5 equiv.) in 15 mL dry Me_2SO and stirred for 2 h. Workup yield an oily residue. By use of toluene as an internal standard, a yield of 3-methyl-3-(diethoxyphosphinyl)-2,2,-diphenylaziridine of 51% was estimated by ^{1}H NMR. The material was chromatographed with

hexane (75%) - ethyl acetate (25%) but remained upon the column from which it was eluded with ethyl acetate to give an oil having FTIR (neat) at 3254 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ 7.61-7.15(m, 10H), 4.04(p, *J*=7.2 Hz, 2H), 3.85-3.75(m, 1H), 3.51-3.49(m, 1H), 2.17(br, s), 1.29(t, *J*=7.2 Hz, 2H), 1.30(d, *J*=5.7 Hz, 3H), 1.028(t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 141.5(d, J_{PC}=2.2 Hz), 140.7(d, J_{PC}= 2.2 Hz), 128.2, 128.0, 127.9, 127.8, 127.1, 126.9, 62.0(d, J_{POC}=7.5 Hz), 61.9(d, J_{POC}=6.5 Hz), 54.1(d, J_{PC}= 2.1 Hz), 40.6(d, $^1J_{PC}$=181 Hz), 17.2, 16.2,(d, J_{PC}=6.0 Hz), 16.0(d, J_{PC}=6.0 Hz); GC and HRMS, m/z, (relative intensity) 345(M^+, 0.9), 344.14107(M-1^+, 2.2, calcd for $C_{19}H_{23}NO_3P$ 344.14155), 208(100), 180(0.8), 165(18), 137(0.6), 105(70), 77(10); GCMS (CI, ammonia), m/z (relative intensity) 346(MH^+, 100), 208(6).

Two trace products, diethyl benzhydrylphosphonate and 2-methyl-3-phenylindole (**6e**), were also separated during the column chromatography. Their NMR spectra were identical to those previously described.

2-Phenyl-3-(diethoxyphosphinyl)indole (**8b**) and 1-hydroxy-2-phenyl-3-(diethylphosphinyl)indole (**8c**)

A mixture of cis-α-nitrostilbene (0.87 mmol) with $(EtO)_2P(O)H$ (0.87 mmol) and potassium carbonate (4.35 mmol) in EtOH was vigorously stirred at 70 °C for 13 h. The mixture was then cooled and poured into cold brine solution and extracted with CH_2Cl_2. The extract was washed, dried, filtered and concentrated to give by NMR (toluene was used as internal standard) **8b** (14%) and **8c** (36%). The material

was chromatographed with hexane (50%) - ethyl acetate (50%) to give the pure products. Compound **8b** had mp 171-174 °C; FTIR (neat) at 3132 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 10.05(br, s), 8.05-7.15(m, 9H), 4.04-3.78(m, 4H), 1.11(t, *J*=7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 145.9, 145.6, 136.3, 136.1, 131.8, 130.3(d, J_{PC}=13.8 Hz), 129.5, 128.7, 128.0, 122.8, 121.3, 111.4, 61.2(d, J_{POC}=21.3 Hz), 16.2(d, J_{PC}=20.4 Hz); GC and HRMS, m/z (relative intensity) 330(12), 329.11761(M^+, 76, calcd for $C_{18}H_{20}NO_3P$ 329.11808), 301(12), 273(7), 255(16), 238(14), 193(100), 178(2), 165(11), 137(4), 77(5); GCMS (CI, ammonia), m/z (relative intensity) 347($M+18^+$, 13), 330($M+1^+$, 100), 193(2), 165(0.2). Elemental analysis calcd for $C_{18}H_{20}NO_3P$: C, 65.65; H, 6.12; N, 4.25; O, 14.57; P, 9.40. Found: C, 65.06; H, 6.24; N, 4.13; P, 8.82.

Compound **8c** had mp 117-118 °C; FTIR (neat) at 2814 cm^{-1} (-OH); ^{1}H NMR ($CDCl_3$) δ 11.26(br, s), 7.82-7.05(m, 9H), 3.72-3.51(m, 4H), 0.929(t, *J*=6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 143.6, 143.3, 134.4, 134.3, 130.7, 128.6, 127.2, 124.8(d, J_{PC}=8.6 Hz), 122.6, 121.5, 120.4, 109.5, 61.6, 15.8; GC and HRMS, m/z (relative intensity) 345.11276(M^+, 100, calcd for $C_{18}H_{20}NO_4P$ 345.11276), 330(12), 329(78), 286(3), 272(6), 255(16), 238(15), 193(100), 165(10), 137(7), 105(3), 77(5); GCMS (CI, ammonia), m/z (relative intensity) 363(M+18, 14), 346(M+1, 90), 330(100), 208(1), 193(2), 165(0.4). Elemental analysis calcd for $C_{18}H_{20}NO_4P$: C, 62.61; H, 5.84; N, 4.06; O, 18.53; P, 8.97. Found: C, 62.65; H, 5.98; N, 4.05; P, 8.82.

Diethyl(1-anilino-2-phenylvinyl)phosphonate(**9**)

Reaction of 0.66 mmol cis-α-nitrostilbene in 2 mL of $(EtO)_3P$ for 3 h gave by NMR with toluene as an internal standard, a 77% yield of **9** after vacuum distillation of the volatiles. Two isomers (capillary column GC) were observed and had FTIR absorption at 3287 and 3173 cm^{-1} (-NH). GCMS indicated that both isomers had the molecular weight of 331. The major isomer had m/z (relative intensity) 331(14), 228(15), 193(100), 165(11), 137(3), 116(11), 104(7), 91(13), 77(12); GCMS (CI, ammonia), m/z (relative intensity) 349($M+18^+$, 19), 331($M+1^+$, 100), 193(14); the second isomer had m/z (relative intensity) 331(45), 240(56), 193(33), 178(28), 165(18), 152(8), 137(23), 109(37), 104(100), 91(20), 77(15); GCMS (CI, ammonia), m/z (relative intensity) 349($M+18^+$, 21), 332($M+1^+$, 100), 193(3). HRMS of the mixture gave m/z (relative intensity) 331.13318(M^+, 61, calcd for $C_{18}H_{22}NO_3P$ 331.13373), 240.0784($C_{11}H_{15}NO_3P^+$, 20), 194.0970($C_{14}H_{12}N^+$, 100). 193.0889($C_{14}H_{11}N^+$, 16), 104.0502($C_7H_6N^+$, 34). All fragments were within 3.0 ppm of the assigned atomic composition. Column chromatography with silica gel and hexane (90%) - ethyl acetate (10%) gave the two isomers in pure form. The isomer eluted first had mp 103-104 °C; FTIR ($CDCl_3$) at 3287 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42-6.57(m, 11H), 5.57(d, J =7.2 Hz, 1H), 4.22-4.01(m, 4H), 1.28(t, J=7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 141.78, 134.02(d), 130.14, 129.95, 128.73, 128.41, 128.09, 125.38, 119.86, 115.74, 62.47(d), 16.27. The second isomer was isolated as an oil, FTIR ($CDCl_3$)at 3173 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.58-7.24(m, 10H), 5.95(s, 1H),

5.17(d, J=6.3 Hz, 1H), 4.05-3.89(m, 4H), 1.17(td, J=7.2, 0.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 138.72, 137.79, 136.01, 128.92, 128.42, 128.29, 127.88, 127.81, 126.85, 115.44(d), 62.90(d), 15.98.

2-Phenylindole (**8a**)[9]

A trace of the 2-phenylindole (**8a**) was isolated from the above reaction by column chromatography. The material had mp 180-184 °C (lit.[9] 188-190 °C); ^1H NMR ($CDCl_3$) δ 8.34(br, s), 7.67-6.83(m, 10H).

Diethyl(2-nitro-1,2-diphenylethyl)phosphonate

cis-α-Nitrostilbene (1 mmol) in 15 mL of Me_2SO was added dropwise to a mixture of $(EtO)_2P(O)H$ (10 mmol) and t-BuOK (5 mmol) in 25 mL of Me_2SO and the resulting solution stirred for 1 h before hydrolysis with brine. The product was extracted with CH_2Cl_2, washed and dried over Na_2SO_4, and concentrated to an oily residue. The NMR with toluene as an internal standard showed that it contained diethyl(2-nitro-1,2-diphenyl)phosphonate (28%). Flash column chromatography using hexane (75%) - ethyl acetate (25%) gave the phosphonate as a solid, mp 173-174 °C (from hexane dichloromethane); ^1H NMR ($CDCl_3$) δ 7.73-7.29(m, 10H), 6.18(dd, J=12.3, 5.7 Hz, 1H), 4.23(dd, J=12.3, 21.9 Hz, 1H), 3.74-3.56(m, 2H), 3.41-3.29(m, 1H), 3.28-3.16(m, 1H), 0.83(q, J=7.2 Hz, 6H); HRMS, m/z (relative intensity) 317.13069($M-46^+$, 100, calcd for $C_{18}H_{22}O_3P$ 317.1302), 289(6), 273(6), 261(19), 181(44), 165(13), 137(13),

109(65); GCMS (CI, isobutane), m/z (relative intensity) 727($2M+1^+$, 2.2), 364($M+1^+$, 21), 317($M-46^+$, 100), 139(1).

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PART II. PHOTOCHEMICAL DEOXYGENATION OF NITRO AND NITROSO COMPOUNDS BY *tert*-BUTYLMERCURY HALIDES IN THE PRESENCE OF IODIDE ION

Photochemical deoxygenation of nitro and nitoso compounds by *tert*-butylmercury halides in the presence of iodide ion

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ABSTRACT

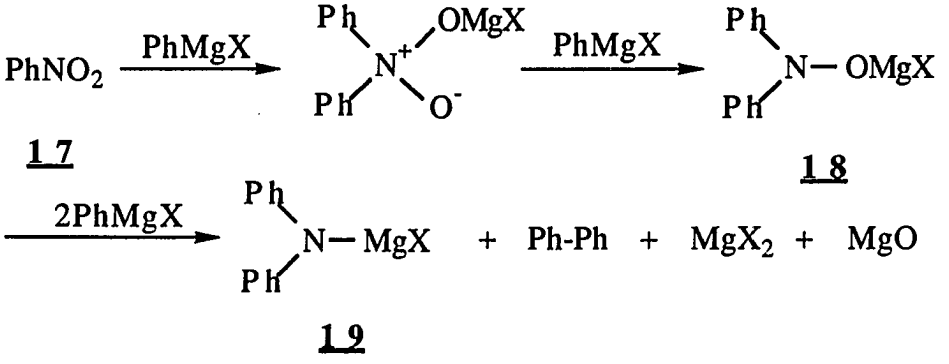
Photolysis of aromatic or β-styrenyl nitro compounds in the presence of *tert*-butylmercury halides and KI in Me_2SO forms products mainly derived from the nitroso compounds. β-nitrostyrenes upon photolysis react with excess *t*-BuHgX and 4-10 equiv. of KI to form PhCH=CHBu-*t* (40%), $PhCH_2C(Ph)=NOBu$-*t* (6%) and $[PhCHC(Ph)N(O)(OBu$-*t*$)]_2$ (44%) (13% and 52% with Dabco or 6% of $PhCH_2C(Ph)=NOBu$-*t* and 48% of isobidesyl with PTSA), $Ph_2C(OBu$-*t*$)CH=NOH$ from $Ph_2C=CHNO_2$ (up to 40% in the presence of PTSA), 3-phenyl-2-(phenylthiyl)indole (68% from $Ph_2C=C(SPh)NO_2$), 2-(*tert*-butylthiyl)-3-phenylindole (53% from $Ph_2C=C(SBu$-*t*$)NO_2$), and a mixture of 2-methyl-3-phenylindole (20%), $Ph_2C=C(CH_3)N(Bu$-*t*$)OBu$-*t* (12%) and $[Ph_2C(OBu$-*t*$)C(CH_3)=N]_2O$ (28%) from $Ph_2C=C(CH_3)NO_2$. With 1.5 equiv. of *t*-BuHgCl/2KI, 2,2-diphenyl-3-(phenylthiyl)-2*H*-azirine is initially formed from $Ph_2C=C(SPh)NO_2$ in 60% conversion (40% yield). Nitroso aromatics react with *t*-BuHgX upon photolysis in Me_2SO to form azoxy compounds but in the presence of KI *t*-BuN(Ar)OH and *t*-BuN(Ar)OBu-*t* are observed. The formation of *t*-BuN(Ph)NOH is favored in the presence of PTSA while the formation of *t*-BuN(Ph)OBu-*t* is favored in the presence of Dabco. Nitrobenzene also reacted with *t*-BuHgI/KI to yield *t*-BuN(Ph)OBu-*t* (up to 72%) and *t*-$BuN(t$-$Bu_6H_4)OBu$-*t* (21%). Reactions of 2- or 4-substituted nitrobenzenes occur to generate *p*-$HOC_6H_4N(Bu$-*t*$)OBu$-*t* (28%), *p*-$NCC_6H_4N(Bu$-*t*$)OBu$-*t* (36%), *p*-$OCHC_6H_4N(O)=NC_6H_4CHO$-*p* (50%), *p*-

$PhCOC_6H_4N(O)=NC_6H_4COPh$-*p* (47%), *p*-$NCC_6H_4N$(Bu-*t*)$NHC_6H_4CN$-*p* (38%), *p*-$Me_2NC_6H_4N$(Bu-*t*)OBu-*t* (34%) and *p*-$Me_2NC_6H_4N$(Bu-*t*)H (21%). *p*-Dinitrobenzene yields *p*-*t*-Bu-$C_6H_4NO_2$ (25%) and *p*-*t*-Bu-C_6H_4N(Bu-*t*)OBu-*t* (20%) while the para halobenzenes yield *p*-BrC_6H_4N(Bu-*t*)OBu-*t* (15%) and *p*-BrC_6H_4N(Bu-*t*)H (25%), *p*-IC_6H_4N(Bu-*t*)OBu-*t* (16%) and *p*-IC_6H_4N(Bu-*t*)OH (28%). *o*-Nitrodiphenylaniline yields a mixture of *o*-$C_6H_4NHC_6H_4NHBu$-*t* (29%) and *o*-$C_6H_4NHC_6H_4$(Bu-*t*)OBu-*t* (17%). *o*-Nitrocinnamaldehyde yielded a mixture of quinoline, 2- and 4-*tert*-butylquinoline (about 50%), while *o*-nitrophenylpyruvic acids gave N-*t*-butoxyoxindole (25%).

INTRODUCTION

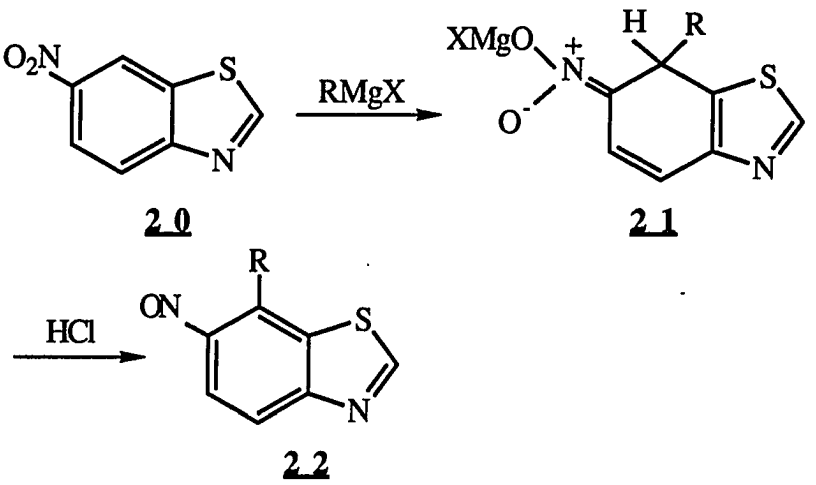
The reaction of alkyl Grignard reagents with nitroarenes have received considerable attention. Gilman and McCracken[1], and later on Kursanov and Solodkov[2], explained the formation of diphenylamine, phenol, and biphenyl from the reaction of PhMgBr, with nitrobenzene in terms of 1,2-addition of PhMgBr to the nitro group, followed by complete reduction to the diphenylaminomagnesium derivative **19** via the hydroxylamine intermediate **18**. The general details of this mechanism were later confirmed by Yost[3], who succeeded in isolating the hydroxylamine in appreciable yields (Scheme I).

Scheme I



In 1976 Bartoli[4] reported the first example of a conjugate addition of an alkyl Grignard reagent to a mononitroarene. The mechanism proposed is given in Scheme II.

Scheme II

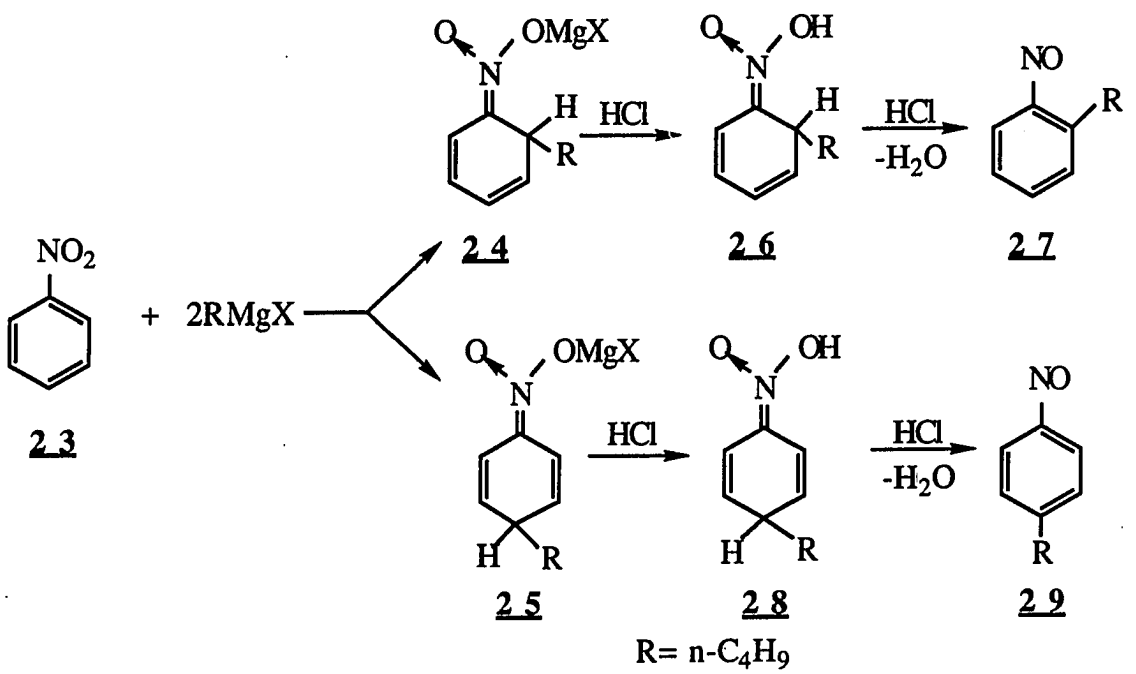


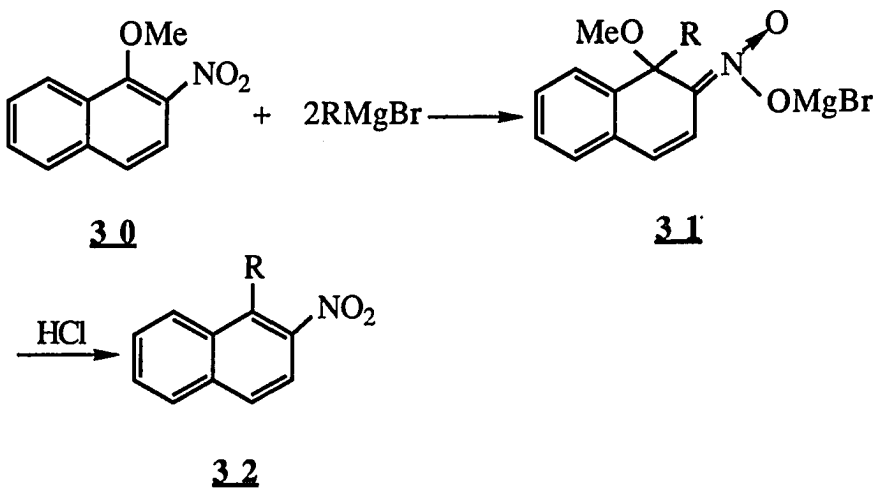
20 21 22

In 1979 Bartoli[5] observed that alkylmagnesium halides reacted with nitrobenzenes and nitronaphthalenes to generate substitution products. (Scheme III).

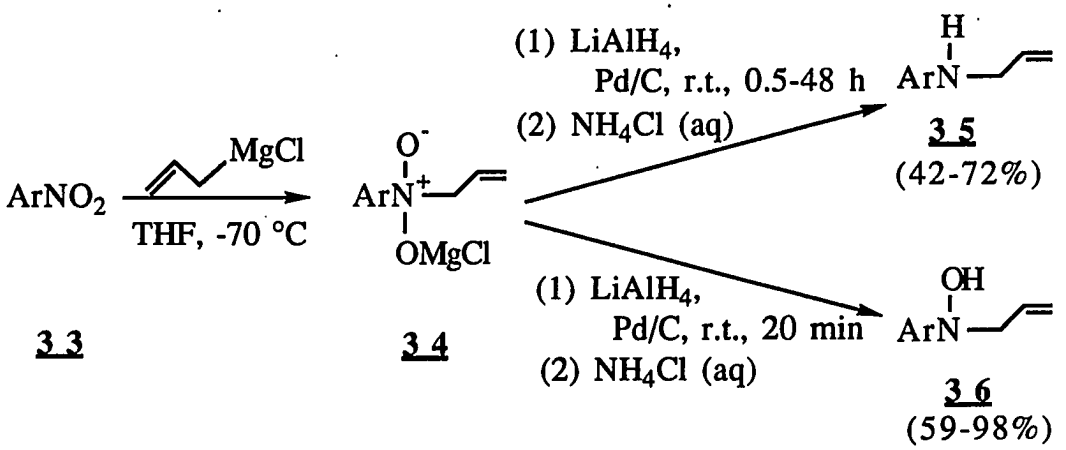
Bartoli[6] reported that allylmagnesium chloride reacted with nitroarenes to form N-allyl-N-arylhydroxylamines and N-allylanilines (Scheme IV).

Scheme III


NO2
+ 2RMgX
OMgX
OH
HCl
HCl
-H2O
NO
R
H
2 3
2 4
2 6
2 7
2 5
2 8
2 9
R= n-C4H9


OMe
NO2
+ 2RMgBr
MeO
R
O
N
OMgBr
3 0
3 1
HCl
R
NO2
3 2

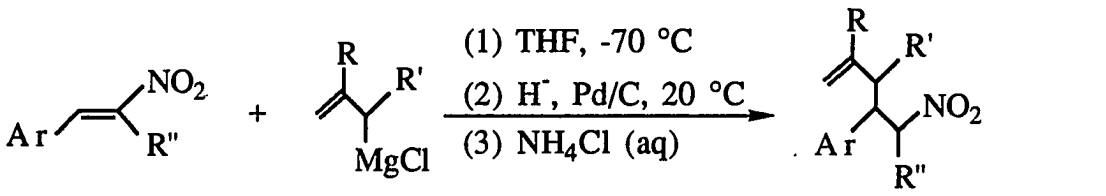
Scheme IV



3 3 3 4 3 5 (42-72%) 3 6 (59-98%)

In 1990 Bartoli[7] observed that allyl Grignard reagents reacted with nitroalkenes to generate addition products (Scheme V).

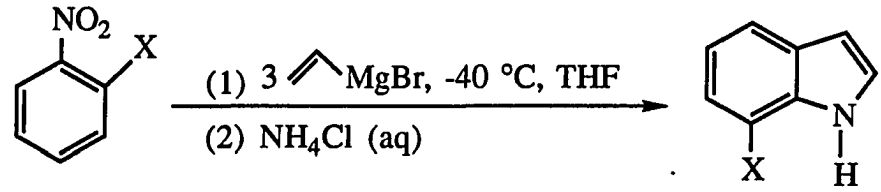
Scheme V



3 7 3 8 (75-84%)

7-Substitution indoles can be synthesized from vinyl Grignard reagents by reaction with 2-substituted nitroarenes (Scheme VI).[8]

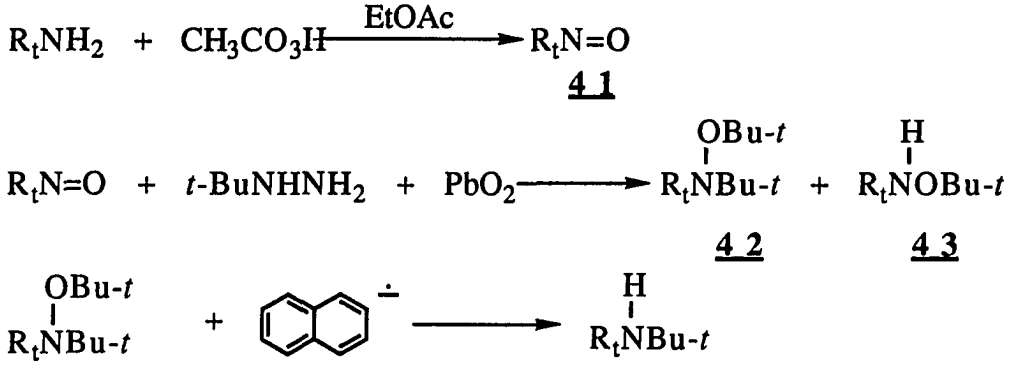
Scheme VI



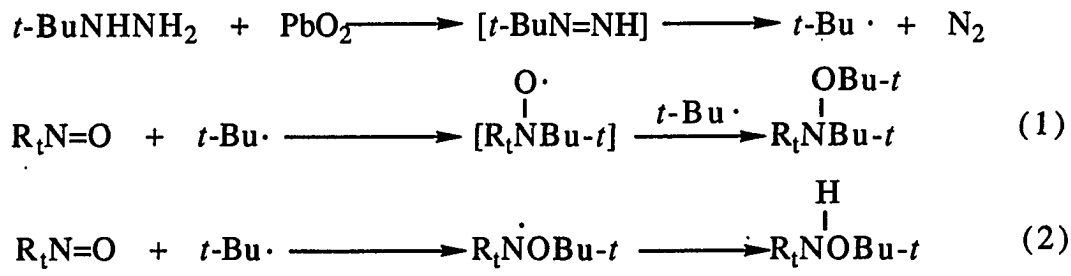
39 40

In 1984 Corey synthesized di-*tert*-alkylamines according to Scheme VII.[9]

Scheme VII



The conversion of the *tert*-alkylamines to the *tert*-alkylnitroso compounds was accomplished by using peracetic acid in ethyl acetate. The *tert*-alkylnitroso compound was then reacted with *tert*-butyl radicals formed from the oxidation of *tert*-butylhydrazine with PbO_2. The major product, tri-*tert*-alkylhydroxylamine 42, and the by-product, O-*tert*-butylhydroxylamine, are explained by reactions 1 and 2.



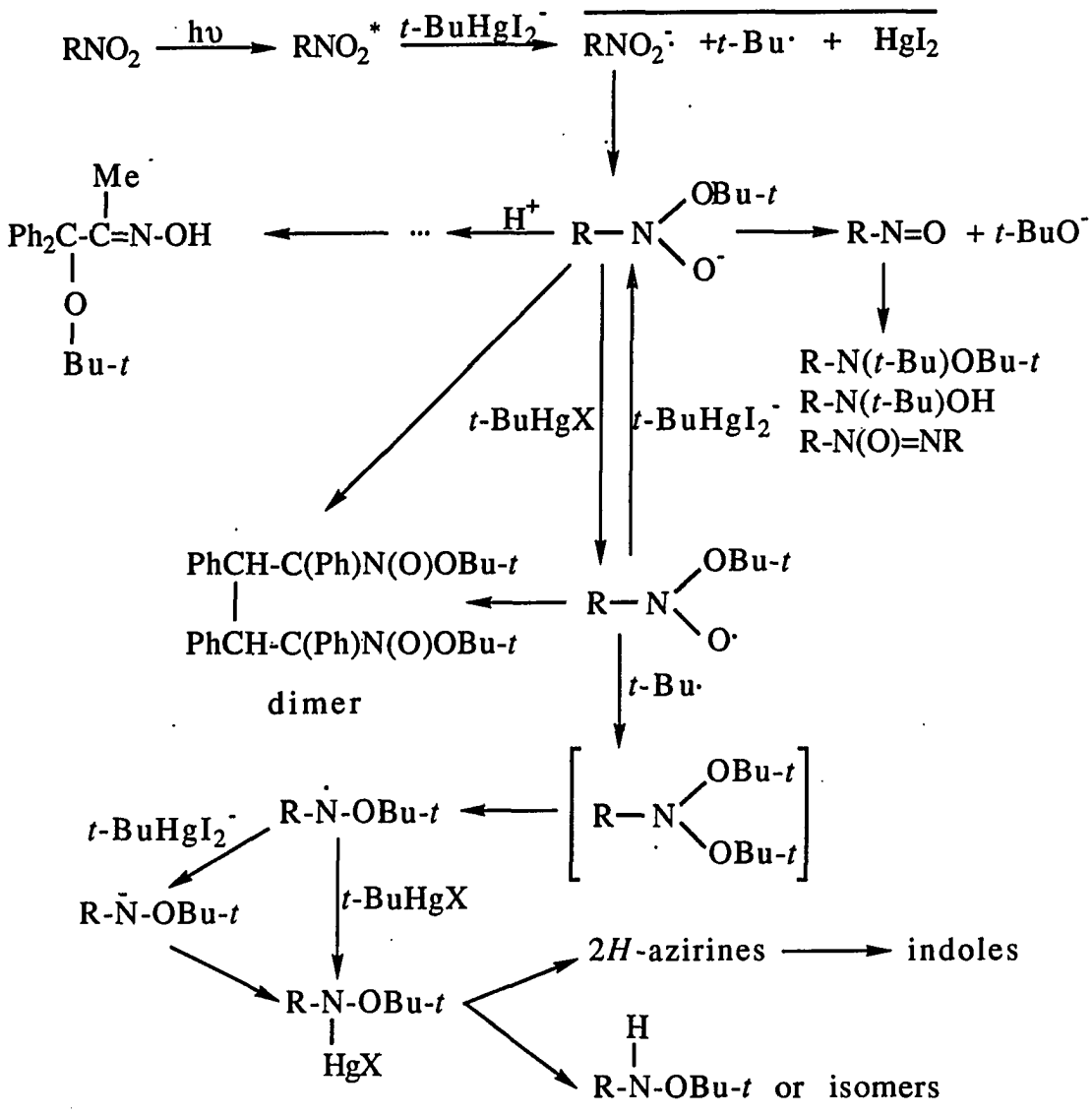
Free radical reactions must be considered in the reaction of nitrobenzene with ogranometallic compounds. Russell[10] observed an ESR signal in the reaction of nitrobenzene with *n*-butyllithium in THF/hexane (3:1). Hoffmann[11] reported that free radicals were identified in the reaction of nitro compounds with organoalkali compounds and Maruyama[12] studied the ESR spectrum of the paramagnetic intermediates formed in the reaction between nitrosobenzene and Grignard reagents. No results have been reported about the reactions of alkylmercury halides with nitro or nitroso compounds. In this section the products and possible reaction mechanism will be discussed for the photochemical reaction of *t*-BuHgX/KI with 1-nitroalkenes and aromatic nitroso or nitro compounds.

RESULTS AND DISCUSSION

The combination of *t*-BuHgI and KI in Me_2SO will reduce enoyl radicals to enolate anions[13] in a process postulated to involve the ate-complex, *t*-$BuHgI_2^-$. This system also photochemically deoxygenates nitroalkenes or aromatic nitro compounds to yield products mainly derived from the resulting nitroso compounds. For nitroalkenes the deoxygenation reactions appear to follow Scheme VIII.

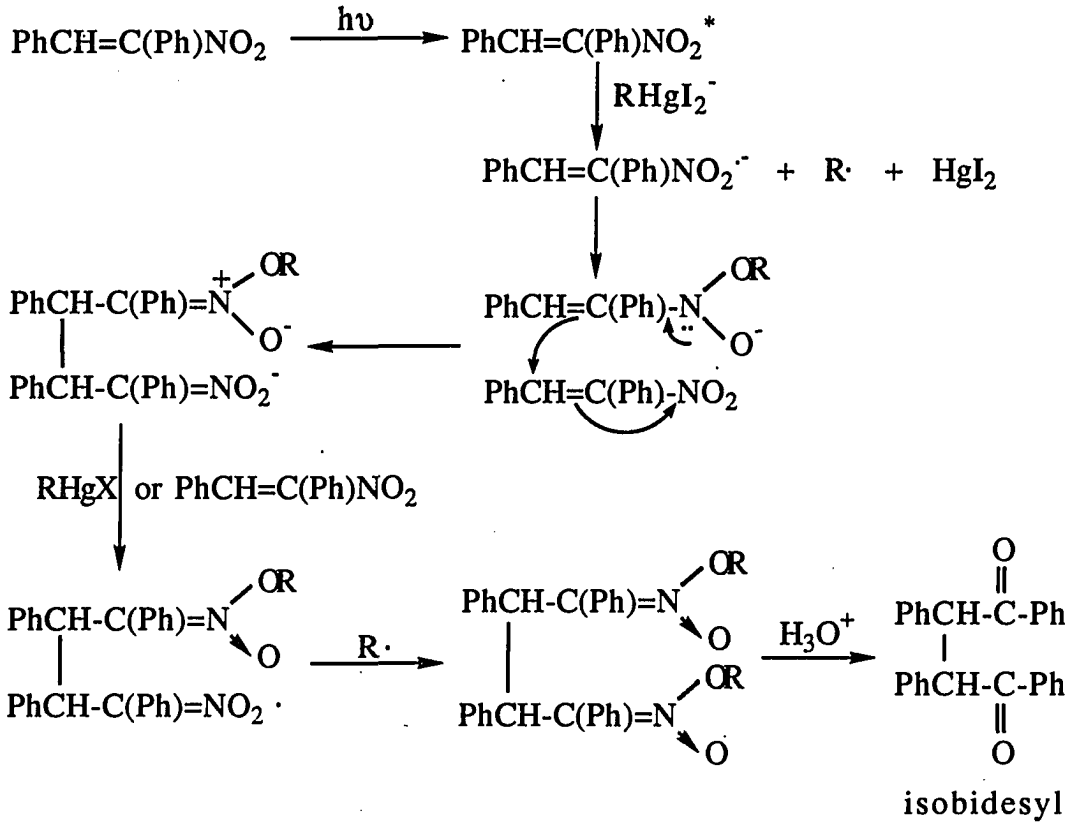
The reactions of β-nitrostyrenes yield a series of interesting compounds depending upon the nature of the α or β substituents. Reaction of β-nitrostyrene with *t*-BuHgX/KI generates in 40% yield the substitution product PhCH=CHBu-*t* (**44**) expected from β-addition of *t*-Bu· followed by loss of NO_2·.[14,16] (*E*)-PhCH=C(Ph)NO_2 reacted with *t*-BuHgI/KI to generate 6% of $PhCH_2C(Ph)$=NOBu-*t* (**45**) and 44% of the dimer $[PhCHC(Ph)N(O)(OBu\text{-}t)]_2$ (**46**). The yields of these two products increased to 13% and 52% when 3 equiv. of Dabco was added. If PTSA was added to the Me_2SO the products were 6% of **45**, a small amount of **46** and 48% of isobidesyl,[15] presumably formed by hydrolysis of **46**. The dimer **46** could be formed by the dimerization of PhCH=C(Ph)N(OBu-*t*)O· (Scheme VIII) or by the process depicted in Scheme IX. A reasonable route to **45** is also shown in Scheme IX.

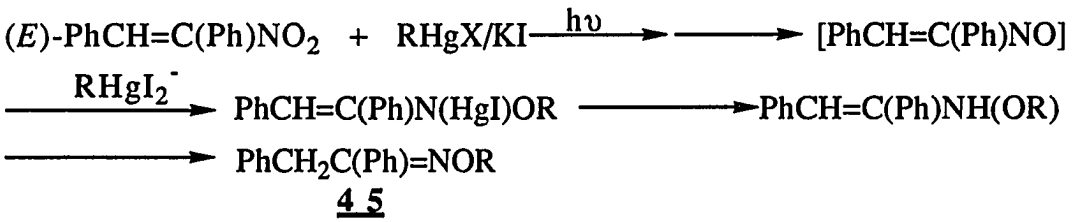
Scheme VIII


RNO2
hυ
RNO2*
t-BuHgI2-
RNO2·- +t-Bu· + HgI2
Me
Ph2C-C=N-OH
O
Bu-t
H+
R—N
OBu-t
O-
R-N=O + t-BuO-
R-N(t-Bu)OBu-t
R-N(t-Bu)OH
R-N(O)=NR
t-BuHgX
t-BuHgI2-
PhCH-C(Ph)N(O)OBu-t
PhCH-C(Ph)N(O)OBu-t
dimer
O·
t-Bu·
R-N-OBu-t
t-BuHgI2-
t-BuHgX
2H-azirines
indoles
HgX
H
R-N-OBu-t or isomers

Scheme IX

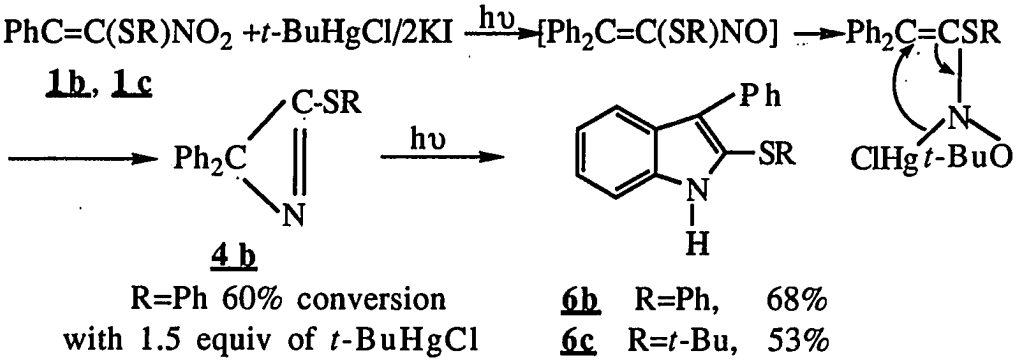
R = *t*-Bu





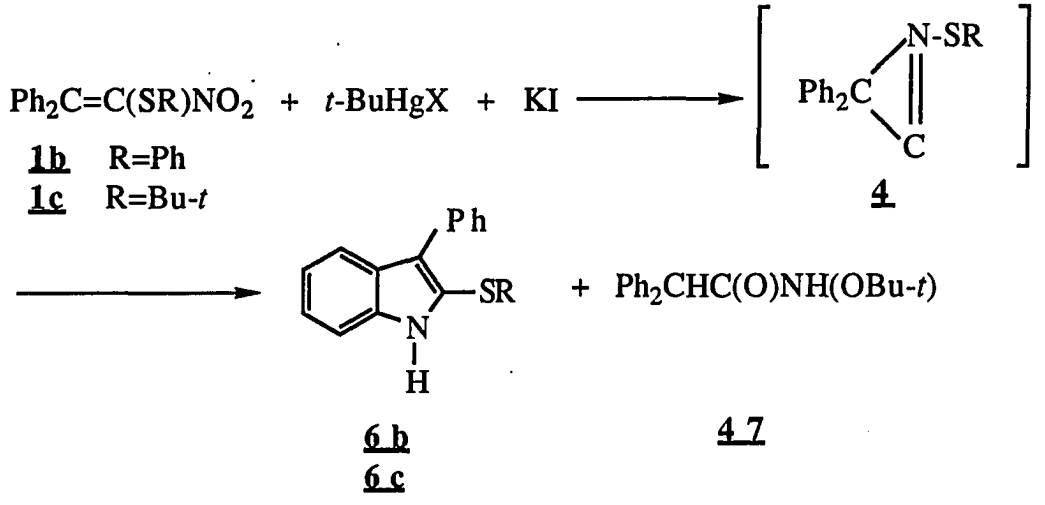
1-Nitro-1-X-2,2-diphenylethylenes fail to form dimers analogous to **46**, presumably because of steric reasons. Instead, they are deoxygenated to yield 2*H*-azirines and/or indoles as shown in Scheme X.

Sheme X



A minor product $Ph_2CHC(O)NH(OBu\text{-}t)$ (**47**) observed from $Ph_2C{=}C(SR)NO_2$ is consistent with the formation of $Ph_2C{=}C(SR)N(HgCl)OBu\text{-}t$ and its hydrolysis to **47** via $Ph_2C{=}C(SR)NHOBu\text{-}t$. Table 1 list the different conditions employed and the products observed for the reaction of $Ph_2C{=}C(SR)NO_2$ with *t*-BuHgX/KI.

Table 1. Photostimulated reactions of *t*-BuHgX with $Ph_2C=C(SR)NO_2$ in Me_2SO[a]



Molar equivalents				Time	% Yield[b]					
Comp	X	*t*-BuHgX:	KI:	(h)	**1b**	**4b**	**6b**	**47**	**6c**	**1c**
1b	-	- :	4 :	25	+	-	-	-	-	-
1b	-	- :	8[c]:	25	+	-	-	-	-	-
1b	Cl	2 :	5 :	13	tr	-	68	10	-	-
1b	Cl	1.5 :	3 :	17	30	40[f]	-	tr	-	-
1b	Cl	1.5 :	3 :	18[d]	tr	total	52	tr	-	-
1c	-	- :	10:	24	-	-	-	-	-	+
1c	I	2 :	- :	28[e]	-	-	-	-	-	+
1c	Cl	3 :	6 :	24	-	-	-	2	10	53
1c	I	3 :	6 :	8	-	-	-	9	53	-

Table 1. (Continued)

[a] 0.1-0.2 M of $Ph_2C=C(SR)NO_2$ in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

[b] By GC and ^1H NMR with toluene as an internal standard after hydrolysis with saturated sodium thiosulfate solution.

[c] 3 Equiv. of $HgCl_2$ was added.

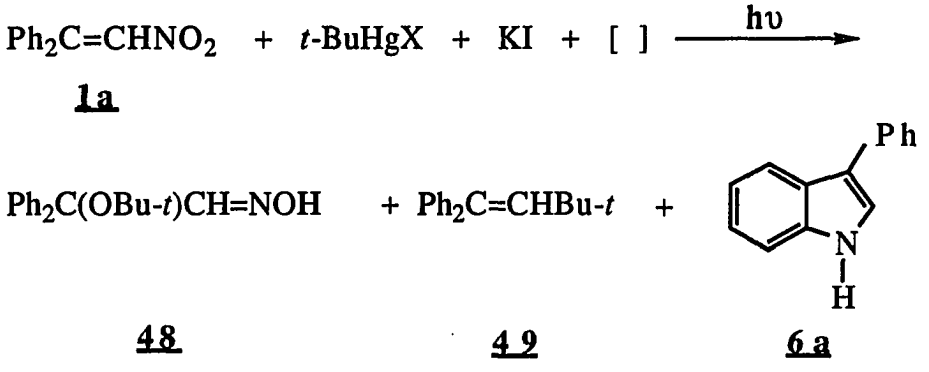
[d] Sunlamp photolysis for 6 h then room light 12 h, total yield of **4b** and **6b** was 52%.

[e] Dark reaction.

[f] GCMS also showed a trace of mw = 375, possible $Ph_2C=C(SPh)NH(OBu\text{-}t)$ or $Ph_2C=C(SPh)N(OH)Bu\text{-}t$ or $Ph_2C(OBu\text{-}t)C(SPh)=NOH$.

1-Nitro-2,2-diphenylethylene (**1a**) and 1-methyl-1-nitro-2,2-diphenylethylene (**1e**) also underwent deoxygenation by *t*-BuHgI/KI to generate indoles and alkoxy oximes (Tables 2 and 3). With **1a** in the presence of PTSA the product $Ph_2C(OBu\text{-}t)CH=NOH$ (**48**) was formed in 40% yield and the substitution product $Ph_2C=CHBu\text{-}t$ (**49**) in 10% yield. With Dabco the yields were only 8% and 14% respectively. Similar results also were observed when **1e** was reacted with *t*-BuHgI/KI (Table 2) except that now the alkoxy oxime was isolated as the dehydration product (**51**). A Possible reaction mechanism is shown in Scheme XI.

Table 2. Photostimulated reactions of *t*-BuHgX with $Ph_2C{=}CHNO_2$ in Me_2SO[a]



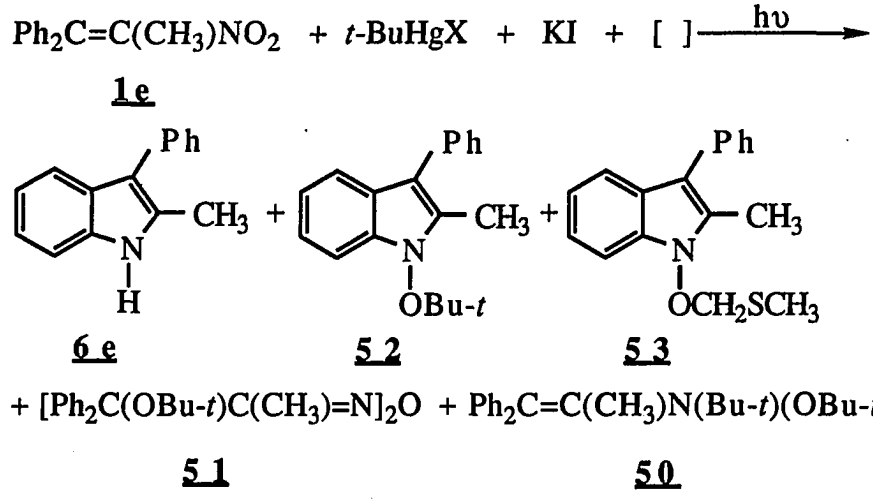
	Molar equivalents				Time	% Yield[b]			
Comp	X	*t*-BuHgX:	KI:	P or D[c]	(h)	1a	48	49	6a
1a	I	2 :	- :	-	26	+	-	-	-
1a	Cl	2 :	4 :	-	8	90	tr	tr	tr
1a	I	2 :	2.5:	-	27	19	8	5	5
1a	I	3.5:	3.5:	3.5(P)	43	-	40	10	tr
1a	I	3 :	3:	3(D)	26	tr	8	14	tr

[a] 0.1-0.2 M of 1a in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

[b] By GC and ^1H NMR with toluene as an internal standard.

[c] (P) means PTSA and (D) means Dabco, which are the chemical reagents for "[ ]" in the reaction.

Table 3. Photostimulated reactions of *t*-BuHgX with $Ph_2C{=}C(CH_3)NO_2$ in Me_2SO[a]



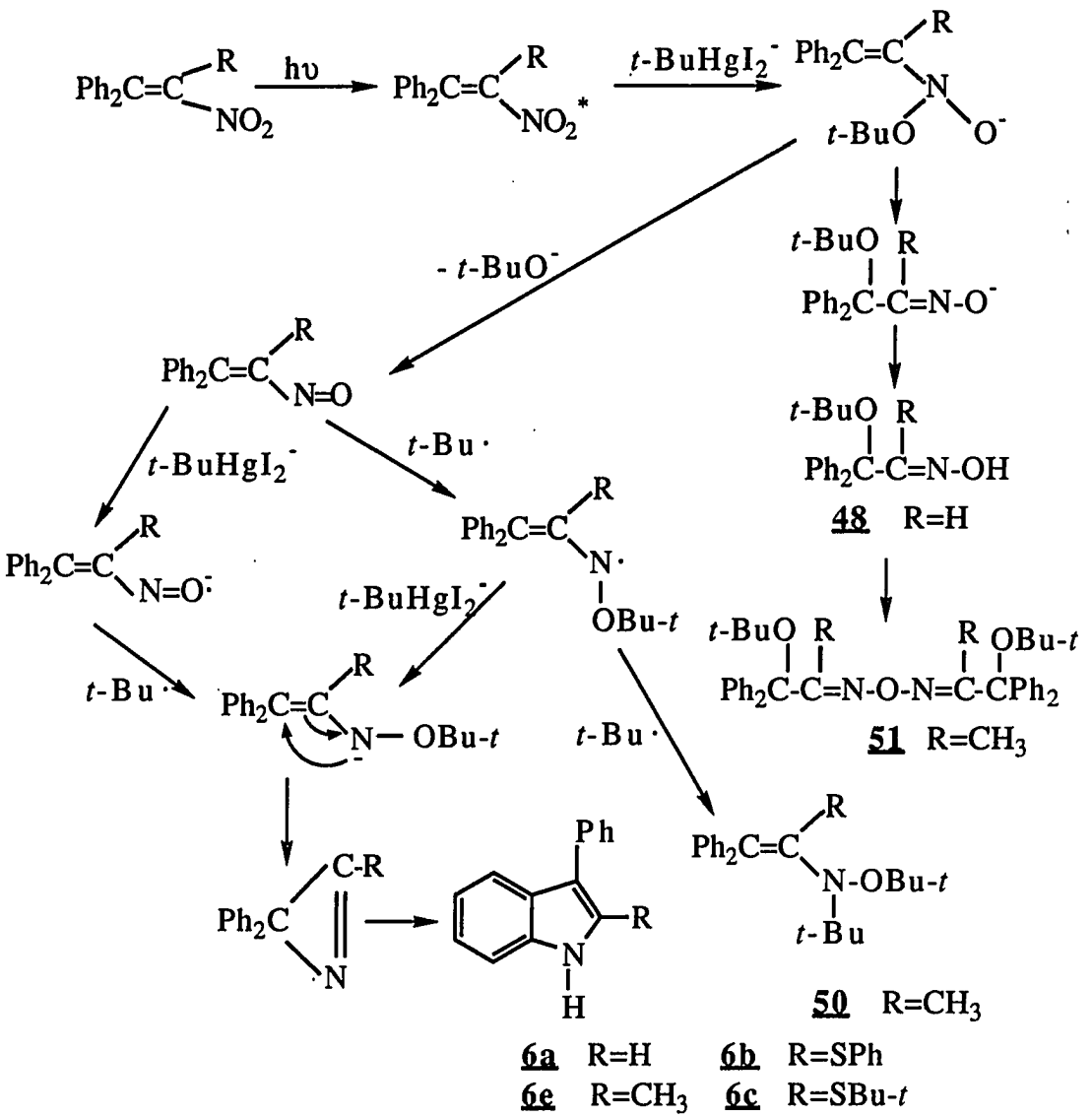
	Molar equivalents				Time	% Yield[b]				
Comp	X	*t*-BuHgX:	KI:	P or D[c]	(h)	50	51	6e	52	53
1e	I	4 :	8 :	4(P)	23	tr	tr	tr	-	-
1e	I	4 :	8 :	-	23	10	20	tr	20	-
1e	I	4 :	8 :	4(D)	17	12	28	20	tr	tr

[a] 0.1-0.2 M of 1e in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

[b] By GC and ^1H NMR with toluene as an internal standard.

[c] (P) means PTSA and (D) means Dabco, which are the chemical reagents for "[ ]" in the reaction.

Scheme XI



The intermediate nitroso compounds derived from the β-nitrostyrenes appear to react preferentially with *t*-Bu· to form the resonance-stabilized alkoxy amino radicals. This is in contrast to the

reaction of PhNO with alkyl radicals where the nitroxide (PhN(R)O·) is observed by ESR spectroscopy. This has been interpreted as preferential attack of R· upon the nitrogen atom. However, attack of R· upon the oxygen atom of PhNO could be a reversible process that is not readily observed by ESR spectroscopy.

Nitrosobenzene upon photolysis with *t*-BuHgCl in Me_2SO generated high yields of azoxybenzene (Table 4). A possible photochemical process is shown in Scheme XII. The product seems to demand that the *t*-Bu· becomes bonded to the oxygen rather than the nitrogen of PhNO. An alternate mechanism might be attack of *t*-Bu· upon PhNO to yield PhN(OBu-*t*) which react rapidly with *t*-BuHgCl to form PhN(HgCl)OBu-*t* and *t*-Bu·.

Scheme XII

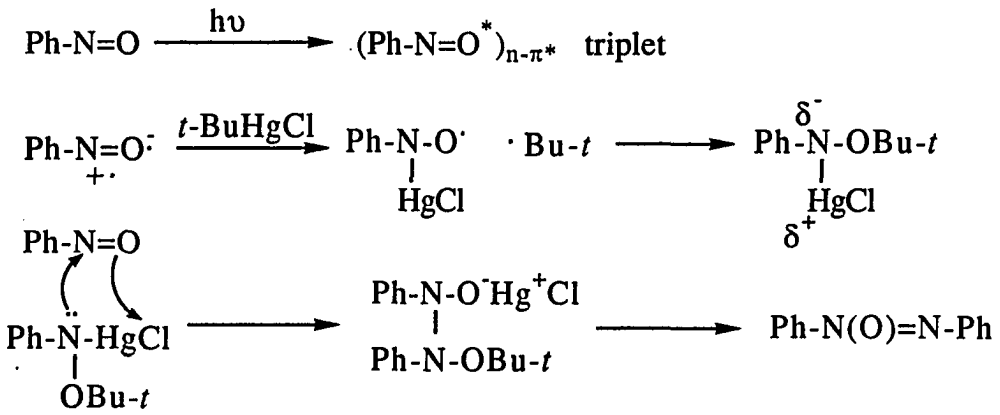
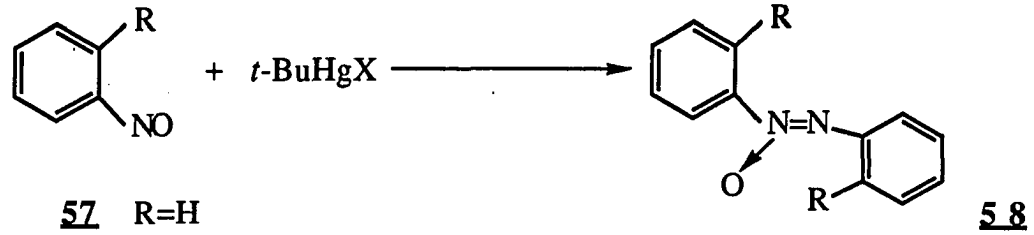


Table 4. Photostimulated reactions of *t*-BuHgX with nitrosobenzene and *o*-nitrosotoluene in Me_2SO[a]



57 R=H
59 R=CH_3

58
60

Molar equivalents			Time (h)	% Yield[b]	
R	X	*t*-BuHgX		**58**	**60**
H	Cl	2	24	98	-
H	Cl	5	24 (dark)	33	-
H	Cl	2	44	100[c]	-
H	I	2	25	90[d]	-
H	I	2	24	63[e]	-
H	I	5	24 (dark)[f]	51	-
CH_3	Cl	2	23	-	50[g]
CH_3	Cl	2	44	-	67[h]
CH_3	I	2	36	-	50

[a] 0.1-0.2 M of nitrosobenzene or *o*-nitrosotoluene in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

Table 4. (Continued)

b By GC or ^1H NMR with toluene as an internal standard.

c Cis/trans ratio = 4:1 by GC.

d Me_2SO 10 mL with 1 mL of TFA, Z:E = 27:1 in GC.

e Me_2SO 5 mL with 5 mL of HOAc.

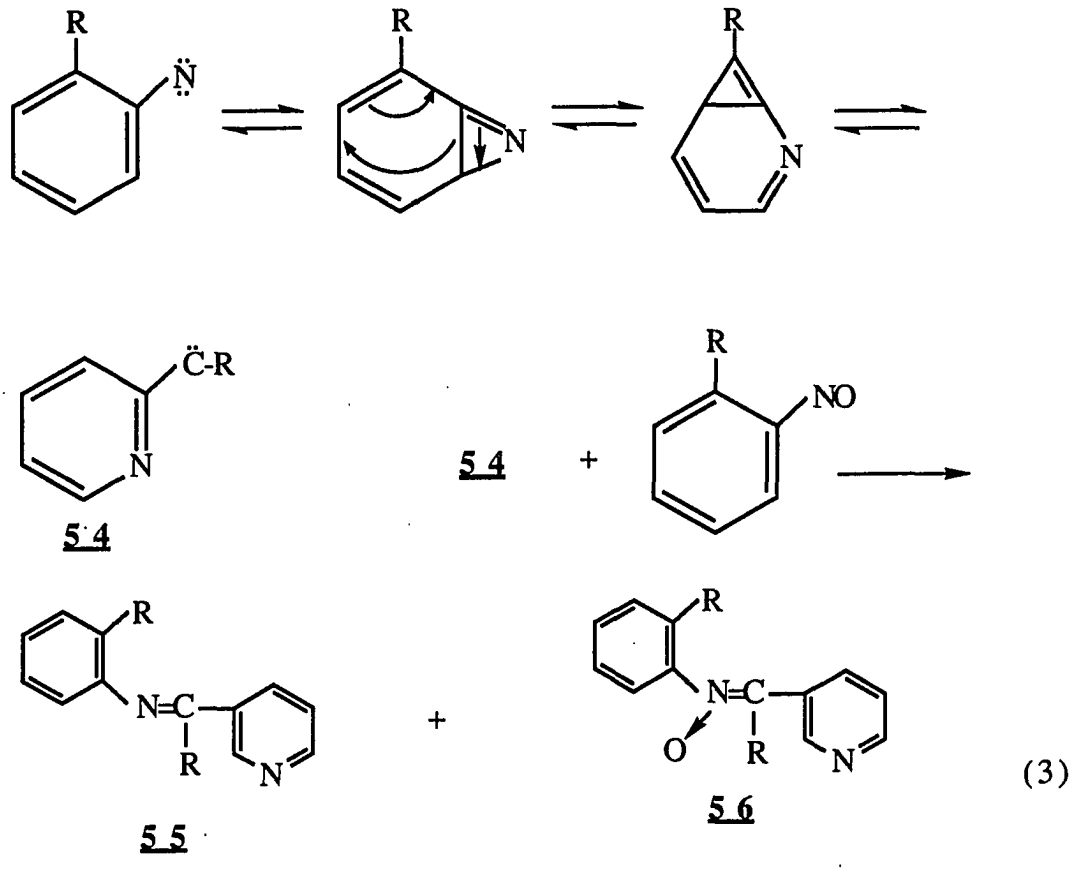
f Trace of unreacted nitrosobenzene left.

g 16% of Unreacted *o*-nitrosotoluene left.

h Cis/trans ratio = 1:7 by GC.

It was reported that deoxygenation of *o*-nitrosotoluene by $(EtO)_3P$ at 0 °C proceed via the nitrene which rearranged to the carbene **54** before coupling with the nitroso compound to form **55** and **56** (reaction 3). Photolysis of *o*-nitrosotoluene with *t*-BuHgX generated *o*,*o*'-dimethylazoxybenzene **60**[17] without the formation of compounds **55** or **56**. Obviously a nitrene is not the precursor to the azoxy compound in the deoxygenation reaction with *t*-BuHgCl. Photolysis of *p*-nitrosodimethylaniline and *t*-BuHgCl gave unreacted *p*-nitrosodimethylaniline and a trace of *p*-nitrodimethylaniline (**61**).

The presence of CH_3CO_2H or CF_3CO_2H did not prevent the formation of the azoxy compounds from PhNO or *o*-MeC_6H_4NO. In the presence of acids presumably PhN(HgX)OBu-*t* is converted to PhNHOBu-*t* which undergoes condensation with unreacted PhNO.



(3)

$RHgI_2^-$ is mild reducing agent which upon photolysis will reduce aromatic nitroso or nitro compounds. Photolysis of nitrosobenzene, *o*-nitrosotoluene and *p*-nitrosodimethylaniline with *t*-BuHgX/KI generates high yields of the N-*tert*-butyl-N-arylhydroxylamines and the N-*tert*-butyl-N-*tert*-butoxyanilines, particularly in the presence of PTSA or Dabco. Similar results were observed when nitrobenzene was photolyzed with *t*-BuHgX/KI/Dabco (or PTSA). Table 5 presents the results observed with PhNO and $PhNO_2$. The mechanism of

nitrobenzene and nitrosobenzene reacting with *t*-BuHgX/KI is proposed to follow Scheme XIII. The yields of *t*-BuN(Ph)OH (**63**) increased in the presence of PTSA and *t*-BuN(Ph)OBu-*t* (**62**) increased in the presence of Dabco, at least when a large excess of *t*-BuHgI was employed. In the presence of Dabco the hydroxylamine **63** is slowly converted to the N,O-di-*tert*-butylated hydroxylamine (**62**) (Table 5). This process does not occur as readily in the presence of PTSA. This reaction may involve the oxidation of the anion of **63** by HgI_2 or HgI to the nitroxide which could be reduced back to **63** by *t*-$BuHgI_2^-$ or converted to **62** by reaction with *t*-Bu·. Excess *t*-BuHgI is required for a reasonable yield of **62** or **63** because an appreciable fraction of the *tert*-butyl radicals formed undergo disproportionation to form isobutane and isobutene. The nitroxide, PhN(R)O·, can be observed by GC and GCMS at short reaction times. In one experiment nitrosobenzene was reacted with *t*-BuHgI/KI/PTSA and the reaction was worked up after reaction times of 4h, 8h, 14h, 24h and 36h. Except for the 36 h reaction, there was one extra peak in the GC which GCMS indicated to be PhN(Bu-*t*)O· (m/z=164). The peak disappeared upon storage of the sample for 2 weeks. The nitroxide, *o*-MeC_6H_4N(Bu-*t*)O· was even isolated in the reaction of *o*-nitrosotoluene. Similar results were also observed when nitrobenzene reacted with *t*-BuHgI/KI/Dabco and the reaction products followed by GC and GCMS. Without hydrolysis, GCMS also indicated the formation of complexes of PhN(R)OR with HgI_2 and RC_6H_4N(R)OR with HgI_2.

Scheme XIII

R=*t*-Bu

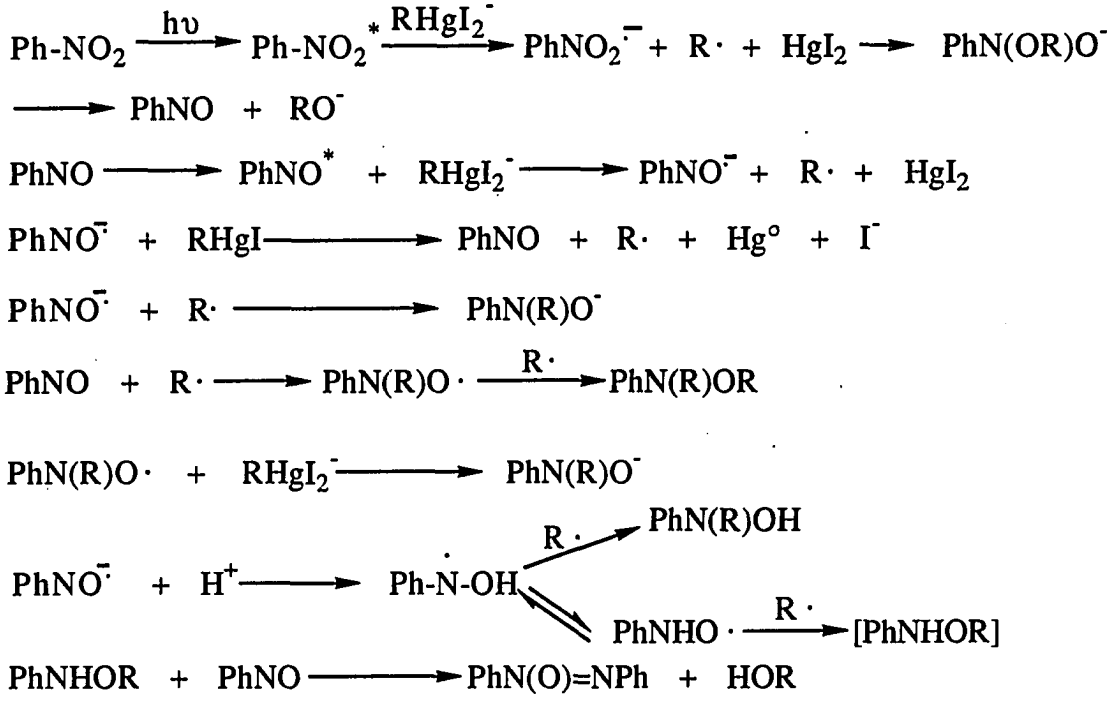
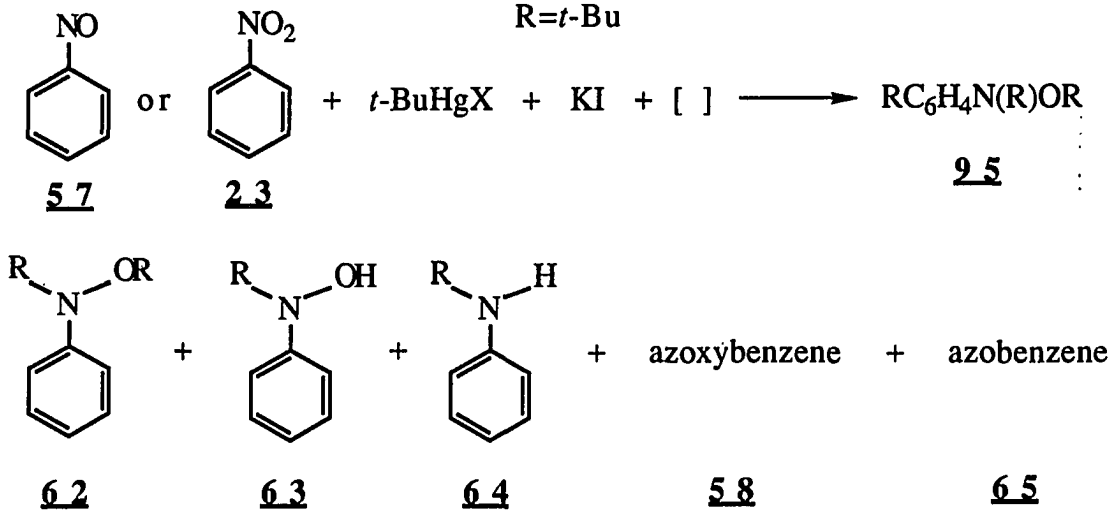


Table 5. Photostimulated reactions of *t*-BuHgX with nitrosobenzene and nitrobenzene in Me_2SO[a]



Comp	Molar equivalents *t*-BuHgX[c]:	KI:	P or D[d]	Time (h)	% Yield[b] 62	63	58	65	95	23
57	2 :	5 :	-	8	24	29[e]	21	7	-	-
57	2 :	5 :	-	24	40	17	28	14	-	-
57	2 :	- :	f	15	20	12	31	25	-	-
57	2 :	4 :	f	15	17	8	33	13	-	-
57	2 :	2 :	3(P)	8	18	73	9	tr	-	-
57	2 :	2 :	3(P)	48	7	47	5	tr	-	-
57	2 :	2 :	3(D)	8	14	55	tr	tr	-	-
57	5 :	5 :	-	36	44	tr	tr	tr	5	-
57	5 :	5 :	-	23[g]	6	-	28	-	-	33
57	5 :	5 :	3(D)	11	56	9	tr	tr	tr	-

Table 5. (continued)

Comp	Molar equivalents *t*-BuHgX[c]:	KI:	P or D[d]	Time (h)	62	63	58	65	95	23
63	5 :	5 :	3(D)	8	65	10	-	-	-	-
63	5 :	5 :	5(P)	12	21	38	-	-	tr	-
63	5 :	5 :	-	36	62	23	-	-	5	-
23	2 :	5 :	-	48	37	6	6	tr	9	35
23	5 :	5 :	-	48	72	tr	-	-	21	-
23	2 :	2 :	3(P)	48	8	4	tr	tr	-	50
23	2 :	2 :	3(D)	31	6	12	tr	tr	tr	46
23	5 :	5 :	5(D)	25	58	39	tr	tr	tr	-
23	5 :	5 :	5 [h]	24	35	-	tr	tr	tr	16

[a] 0.1-0.2 M of 57, 63 or 23 in 1-10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

[b] By GC and ^1H NMR with toluene as an internal standard.

[c] X=Cl in the first four rows, X=I in the other rows.

[d] (P) means PTSA and (D) means Dabco, which are the chemical reagents for "[ ]" in the reaction.

[e] Compound 63 partially decomposes to compound 64 under GC condition or upon distillation.[19,20]

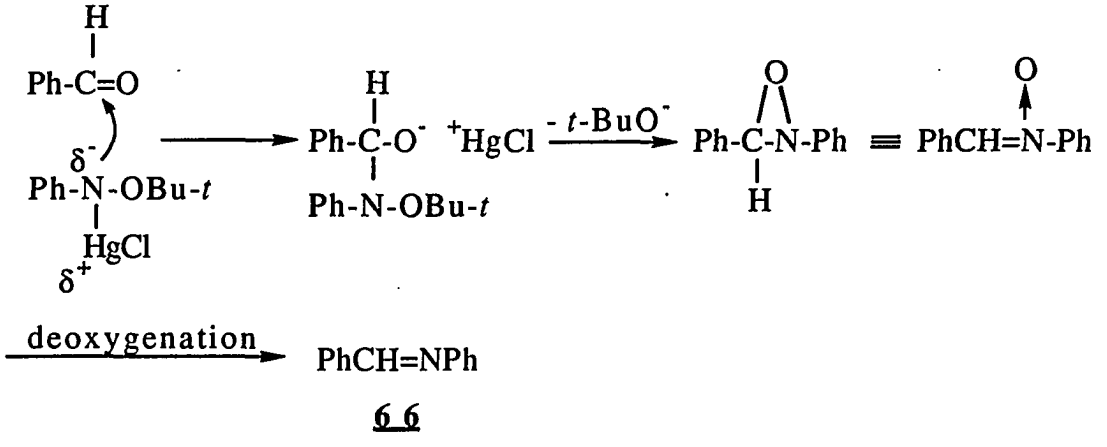
[f] 2 Equiv. of $(CH_3)_3COK$.

[g] Dark reaction with 32% of nitrosobenzene recovered.

[h] 5 Equiv. of $K_2S_2O_8$.

Nitrosobenzene can be used as a dienophile in a photochemical Diels-Alder reaction with 1,3-cyclohexadiene to generate high yields of 2-oxa-3-azabicyclo[2.2.2]oct-5-ene (>95%) in Me_2SO. *t*-BuHgX in Me_2SO with or without KI reacted with nitrosobenzene slowly compared to the Diels-Alder reaction because the product was still 2-oxa-3-azabicyclo[2,2,2]oct-5-ene (85%) and only trace amounts of reduced products were observed. Photolysis of nitrosobenzene with *t*-BuHgX/KI and benzaldehyde gave N-benzylideneaniline (**66**) in 26% yield and azoxybenzene (**58**) in 22% yield when X=I. With X=Cl the yields of **66** was 11% and **58** was 63%. As shown in Scheme XIV, it is proposed that PhCHO can trap the intermediate PhN(HgCl)OBu-*t*.

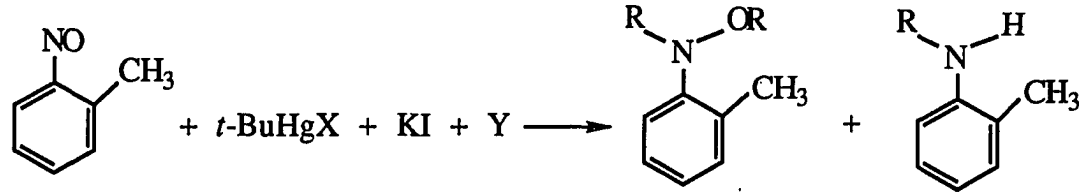
Scheme XIV



66

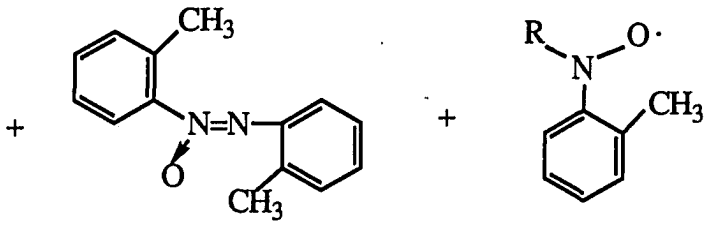
o-Nitrosotoluene and *p*-nitrosodimethylaniline also reacted with *t*-BuHgX/KI to generate reduced products. Mono *tert*-butylated hydroxylamines were not observed but the anilines **68** and **72** were important products. Possibly ArN(HgX)OBu-*t* was an intermediate

which reacted with the nitroso compound to form the azoxy compound or underwent α-elimination to form ArN̈: which was rapidly trapped by *t*-BuHgX to form ArN(HgX)Bu-*t* which yielded the aniline upon hydrolytic workup. Compound **73b** is believed to be formed by the deoxygenation of compound **73a**[18] followed by photolysis.



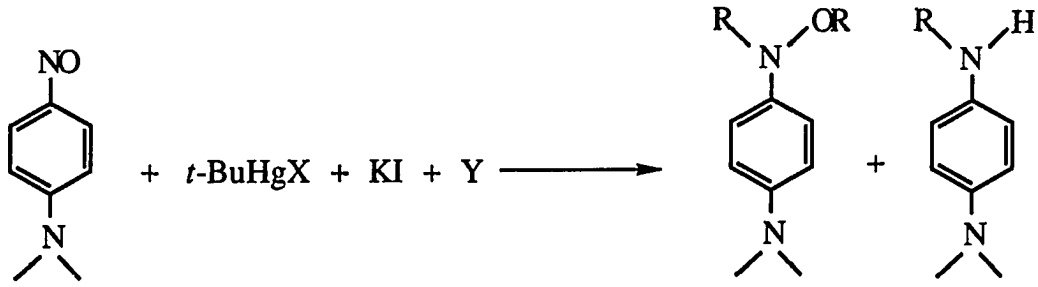
59 R=*t*-Bu **67** **68**

X=Cl		*(1:2:5 and 39 h)	38%	28%
X=I	Y=PTSA	(1:5:5:5 and 36 h)	9%	10%

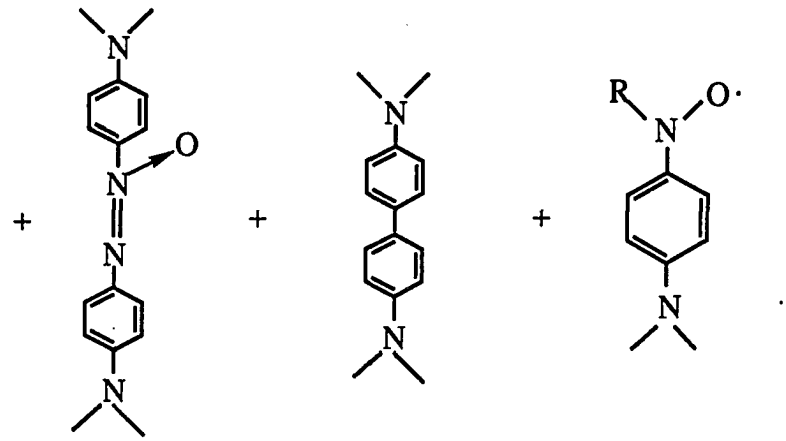


60	**69b**
13%	tr
4%	-

* 1:2:5 Represents the ratio of the equivalents of the reactants and 39 h means reaction time.



70	R= *t*-Bu	71	72
X= Cl	(1:2:5 and 25 h)	28%	12%
X= I Y=Dabco	(1:4:10:3 and 12 h)	34%	21%
X= I Y=PTSA	(1:4:10:3 and 6 h)	-	36%



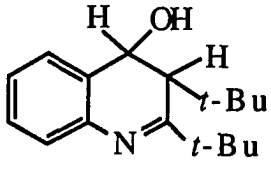
73a	73b	74
11%	5%	tr
14%	tr	tr
8%	tr	tr

Mono-, di- and trisubstituted nitrobenzene derivatives have been used as substrates to react with Grignard reagents.[5,7,8] Photochemical reaction of 2- or 4-substituted nitrobenzenes with *t*-BuHgX/KI in Me_2SO can yield a variety of products as shown in the reactions, which are list in the following pages (pp 90-93).

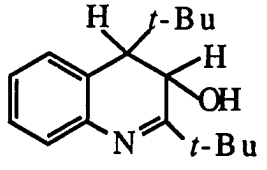
The mechanism of these reactions $XC_6H_4NO_2$ with *t*-BuHgX/KI can be explained as shown in Scheme XV.

2-Substituted nitroarenes are useful reagents for the synthesis of indoles (Scheme VI). Photolysis of *o*-nitrophenylpyruvic acid with *t*-BuHgCl and KI in Me_2SO yielded N-*tert*-butoxyoxindole (**108**) in 25% yield while photolysis of *o*-nitrocinnamaldehyde produced quinoline, 2- and 4-substituted quinoline in about 50% total yield. The mechanism proposed is shown in Scheme XVI.

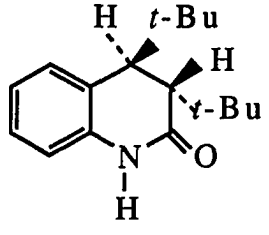
To prove the above mechanism quinoline N-oxide was photolyzed with *t*-BuHgCl/KI in the presence and absence of PTSA. The reaction produced quinoline, mono- and dialkylated quinoline (total about 36%) and about 22% of a di-*tert*-butylated derivative assigned structure **109a**.



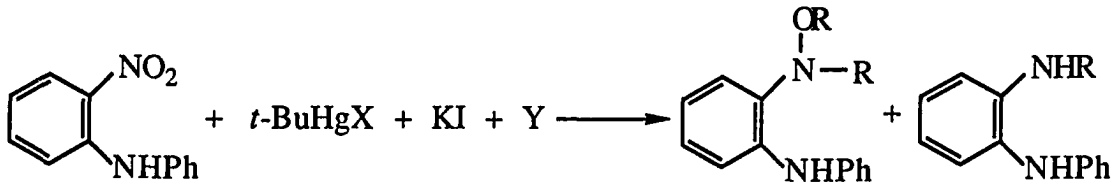
109a
mp: 124-125 °C



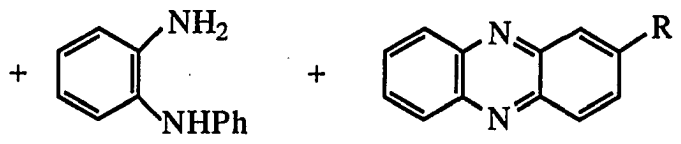
109b



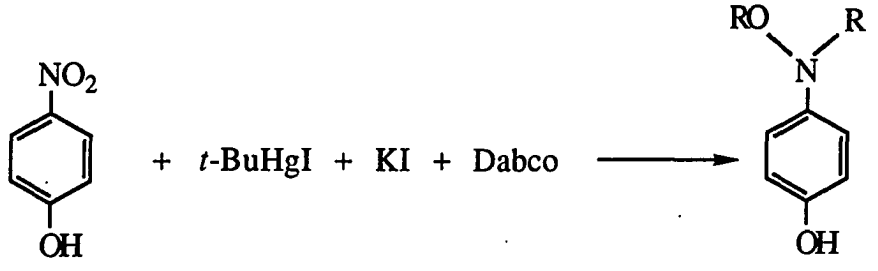
109c
mp: 144-147 °C



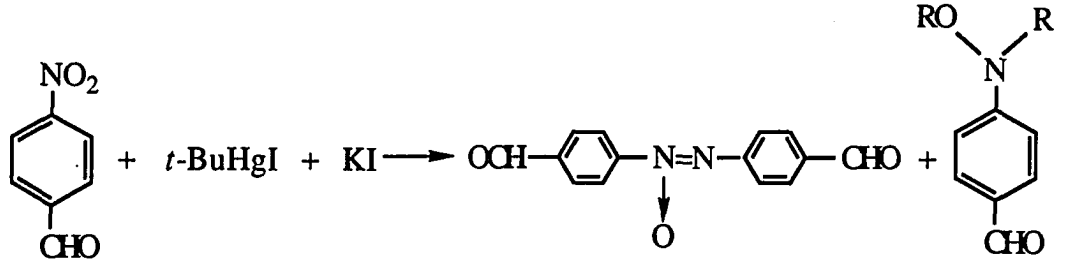
75			76	77
X= Cl		(1:4:10 and 23 h)	17%	29%
X= I	Y=Dabco	(1:4:10:4 and 23 h)	28%	13%



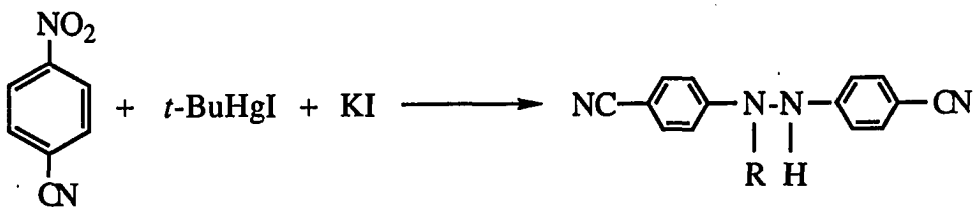
78	79	
7%	-	R=*t*-Bu
tr	tr	



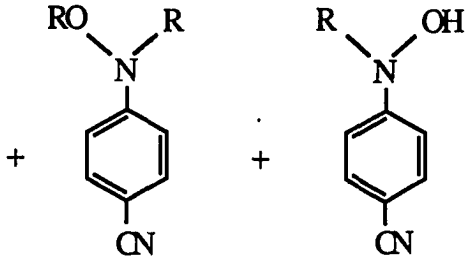
80 (1:2:2:1 and 38 h) 81 (28%)



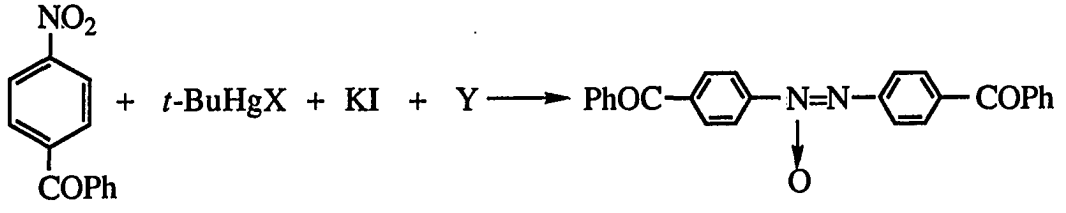
82 (1:2:5 and 48 h) 83 (56%) 84 (4%)



85 (1:4:10 and 24 h) **86** (38%)

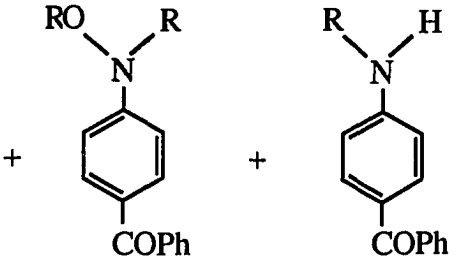


87 (36%) **88** (15%) **R=*t*-Bu**



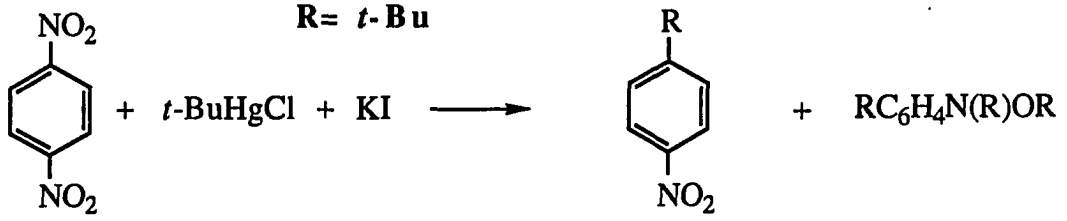
89 **90**

X=Cl	Y=Dabco	(1:5:10:5	and 39 h)	14%
X=I		(1:4: 5	and 48 h)	47%

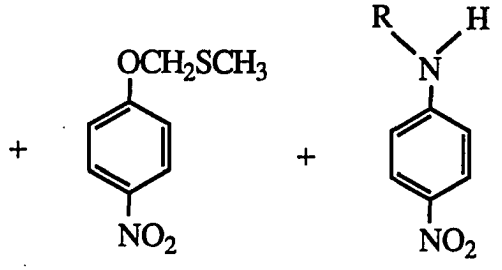


91 **92**

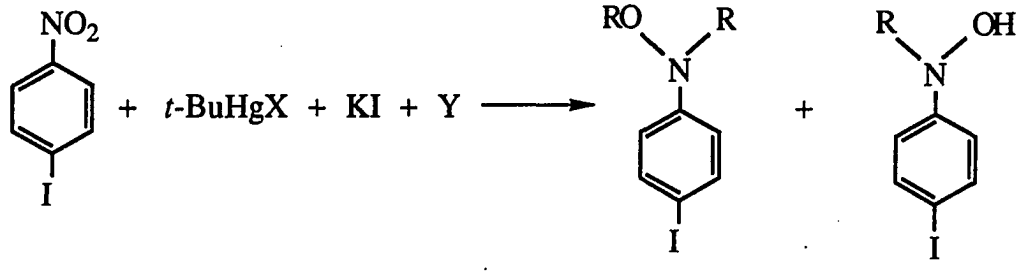
10% 10%
23% 20%



93 (1:4:10 and 36 h) **94** (25%) **95** (20%)

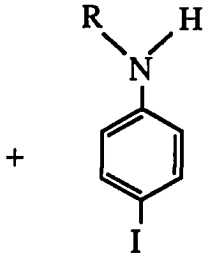


96 (19%) **97** (5%)

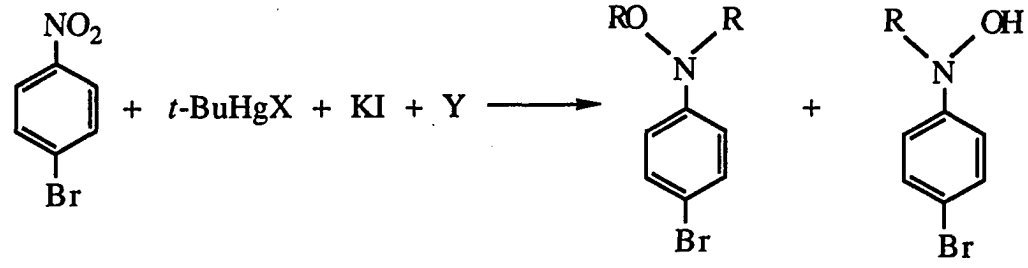


98 **99** **100**

X=Cl	Y=Dabco	(1:5:10:5	and 38 h)	8%	19%
X=I		(1:3: 6	and 23 h)	6%	12%
X=I	Y=Dabco	(1:5:5:5	and 30 h)	16%	28%
X=I	Y=PTSA	(1:5:5:5	and 30 h)	20%	13%

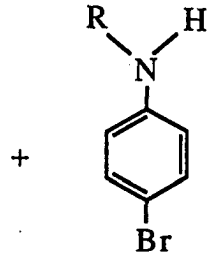


101			**102**
2%			tr
7%	+	$RC_6H_4NO_2$	6%
6%			10%
tr			tr



103 **104** **105**

X=Cl		(1:3:6	and 37 h)	9%	-
X=Cl	Y=Dabco	(1:5:5:5	and 30 h)	6%	18%
X=I		(1:3:6	and 23 h)	8%	-
X=I	Y=Dabco	(1:5:5:5	and 30 h)	15%	25%

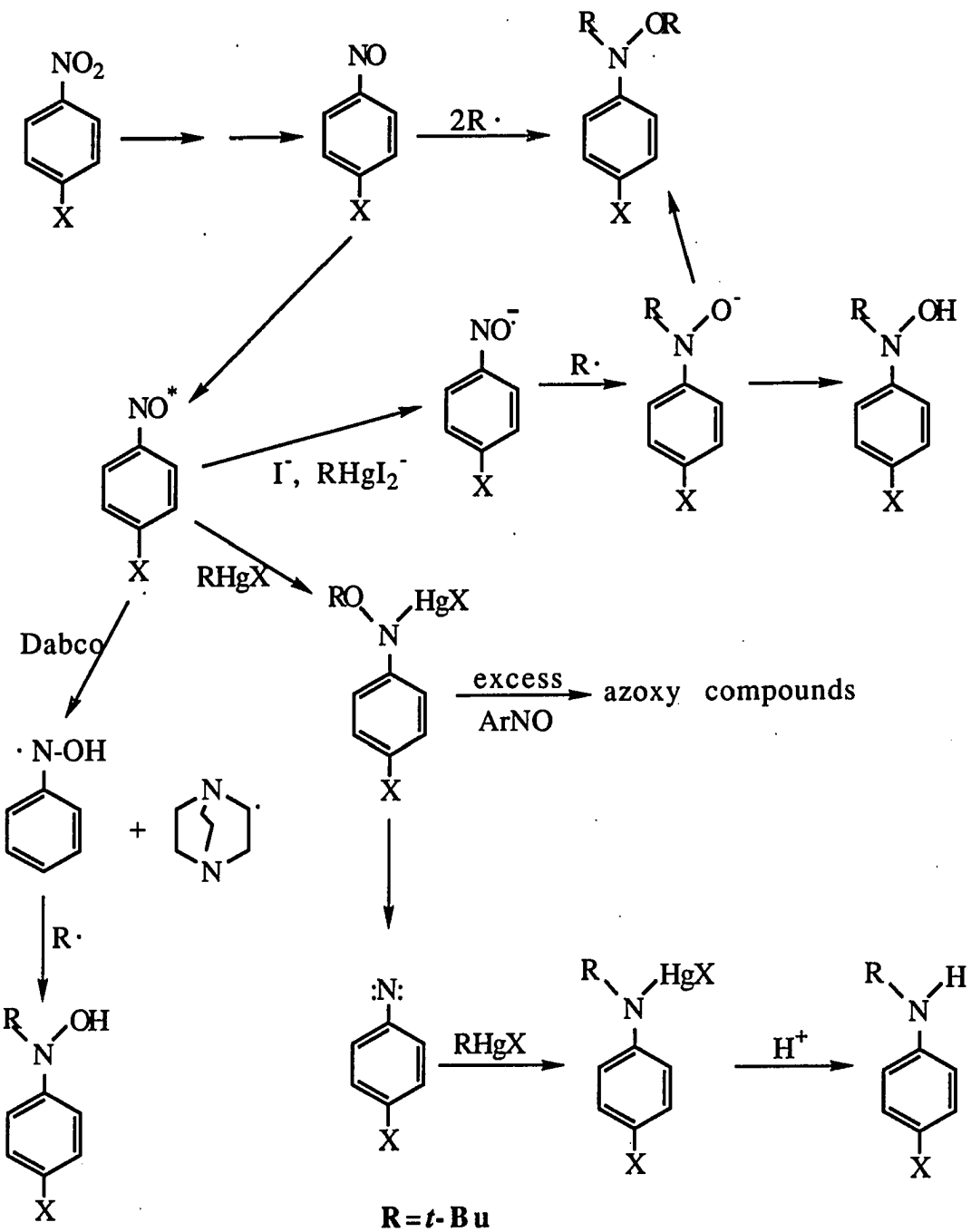


+ + $RC_6H_4NO_2$

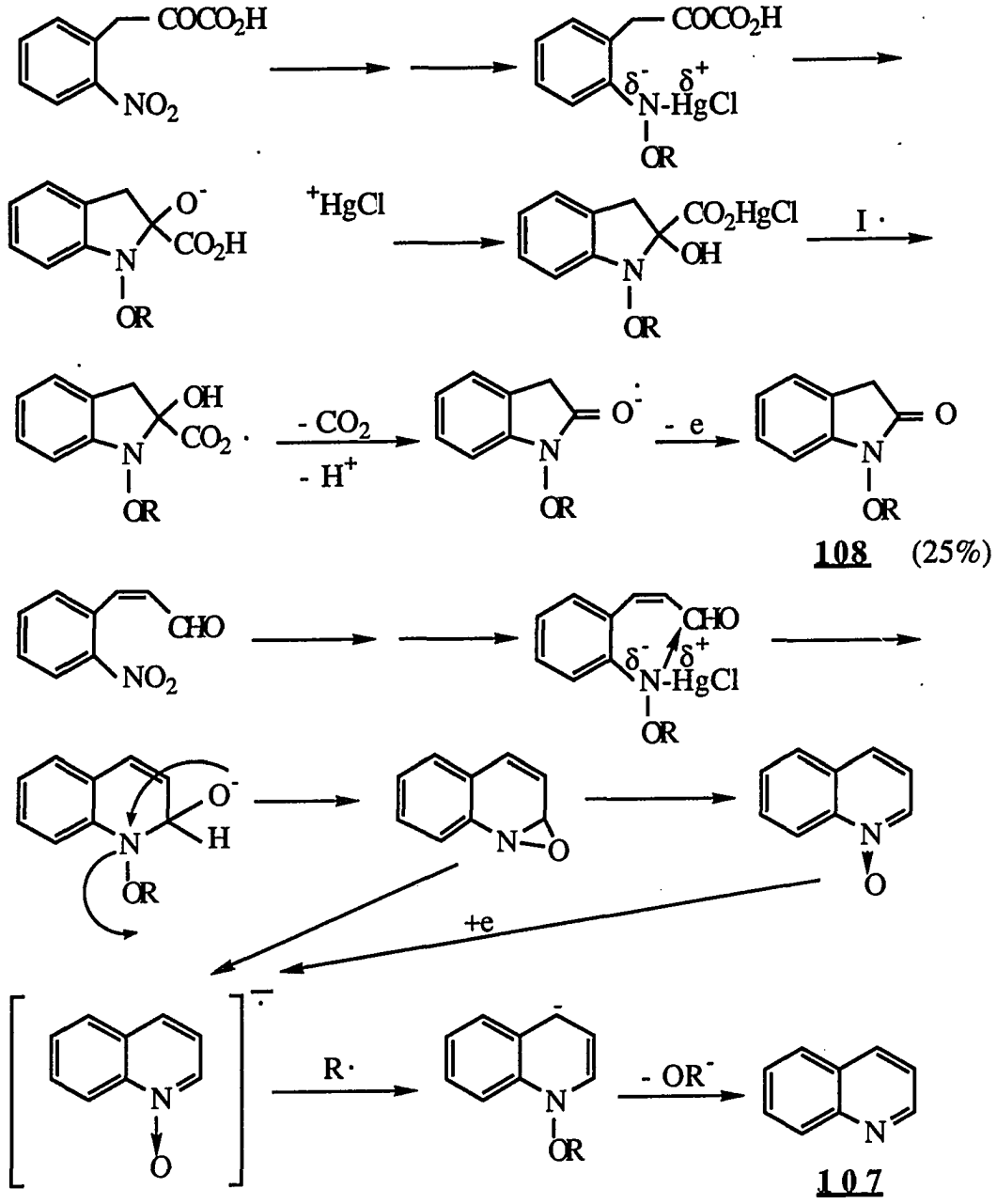
106 **102** **R=*t*-Bu**

15%	15%
-	3%
14%	tr
-	7%

Scheme XV


NO2
NO
2R·
R
N
OR
X
NO*
NO-
R·
O-
OH
I-, RHgI2-
RHgX
RO
HgX
Dabco
excess
ArNO
azoxy compounds
·N-OH
+
N
R·
:N:
RHgX
H+
H
R = t-Bu

Scheme XVI



108 (25%)

107

An isomer of **109a**, compound **109c** was formed in 24% yield from the photolysis of 2-hydroxyquinoline with *t*-BuHgCl/KI/Dabco (1:4:10:5). Compound **109a** and **109c** were not interconverted by treatment with PTSA in Me_2SO and cannot be simple enol-keto tautomers.

Structure **109a** is a rather surprising product from a reaction of quinoline N-oxide. However, the following spectroscopic data seems to demand either structue **109a** or **109b**.

(a) a normal aromatic ring in ^1H (δ^H=7.2-7.4) and ^{13}C NMR

(b) two *tert*-butyl groups, one attached to a satruated carbon (δ^H=0.9) and one attached to a vinyl carbon or a heteroatom (δ^H=1.3)

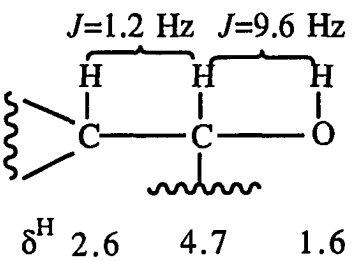
(c) two methine carbons (doublets in ^{13}C NMR) at δ 61.3 and 54.5

(d) a saturated methine carbon containing a heteroatom substituent at δ^H= 4.7

(e) a hydroxy group at 3281 cm^{-1}

(f) probably a C=N group at 1614 cm^{-1}

(g) the partial structure based on ^1H NMR coupling constants, in the presence of D_2O the δ=1.6 hydrogen and the coupling with *J*=9.6 Hz disappear

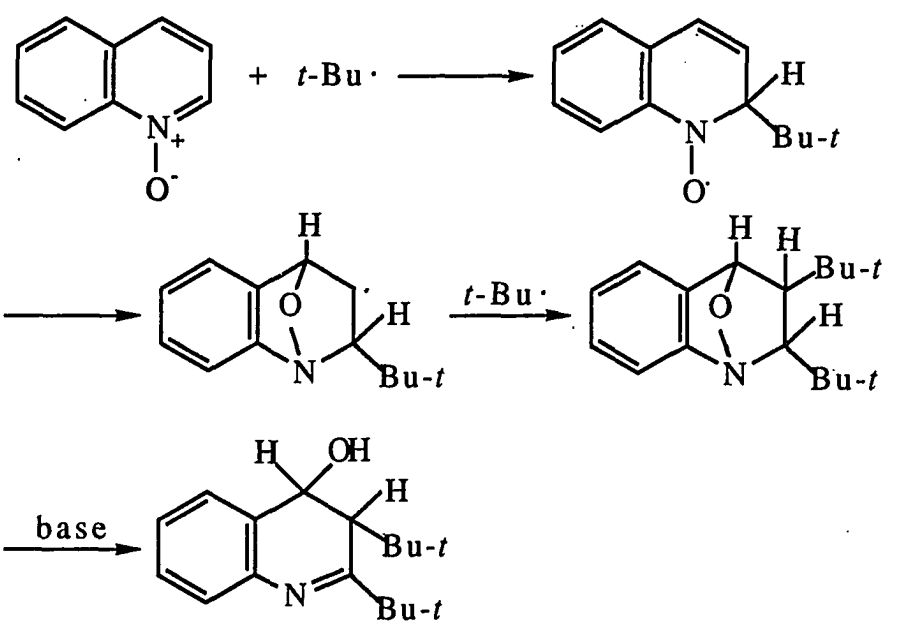


(h) CI and EI MS consistent with the formula weight of 259, HRMS and

elemental analysis consistent with the composition $C_{17}H_{25}NO$.

If the quinoline ring is retained, only structures **109a** and **109b** are possible. Structure **109b** should readily lose H_2O to form 2,4-di-*tert*-butylkquinoline. However, **109a** was stable to GC conditions and even in MS the molecular ion of 2,4-di-*tert*-butylquinoline was not observed. Compound **109a** probably does not lose H_2O readily because the product would be a severely crowded ortho di-*tert*-butylquinoline. A reasonable mechanism for the formation of **109a** is given in Scheme XVII.

Scheme XVII



109a

CONCLUSION

Nitroarenes, nitrosoarenes or the β-nitrostyrenes $PhC(Z)=C(Y)NO_2$ undergo photostimulated reactions with *tert*-butylmercury halides in the presence of iodide ion. A variety of products have been observed which appeared to be formed by ionic and free radical reactions of the intermediates RN(OBu-*t*)OHgX, RNO, RN(OBu-*t*)HgX and RN(Bu-*t*)HgX. Among the novel products isolated from the β-nitrostyrenes are dimeric *tert*-butyl bis-nitronic esters (Z=H, Y=Ph), α-*tert*-butoxyoximes (Z=Ph, Y=H, CH_3), O-*tert*-butyloximes (Z=Y=Ph), 3-substituted 2,2-diphenylazirines (Z=Ph, Y=SPh) and 2-substituted 3-phenylindoles (Z=Ph, Y=*t*-BuS, PhS). Reaction of *t*-BuHgCl with ArNO produces the azoxy compounds by coupling of ArNO with the intermediate ArN(OBu-*t*)HgX. Nitrenes can be excluded as intermediates in the formation of the azoxy compounds. Reaction of *t*-BuHgI/KI with $PhNO_2$ produces a mixture of the azoxy compound and the phenylhydroxylamine derivatives PhN(OBu-*t*)Bu-*t* and PhN(OH)Bu-*t*. N-*tert*-Butylarylamines are also observed with some substituted nitrobenzene derivatives.

EXPERIMENTAL SECTION

Instrumentation and techniques

Analytical gas chromatography was performed using a Varian 3700 gas chromatography equipped with Hewlett-Packed 3390A integrator. ^1H NMR spectra were recorded on a 300-MHz Nicolet NT 300 spectrometer with tetramethylsilane as the integral standard. GCMS were recorded on a Finnegan 4000 spectrometer and HRMS were recorded on a AEI MS 902 mass spectrometer. Melting points were determined on a Thomas-Hoover capillary melting poing apparatus and were uncorrected.

GC yields were determined by using an internal standard (biphenyl or toluene) and were corrected with predetermined response factors. ^1H NMR spectroscopy yields were determined by integration with a known amount of toluene as internal standard.

Solvent and chemical reagents

Solvents were purchased from Fisher and Baker. Dimethyl sulfoxide (DMSO) was distilled from calicum hydride. Other solvents were purchased and used without purification. Me_2SO-d_6 was purchased from Cambridge Isotope Laboratories and dried over 4A molecular sieves. (*E*)-PhCH=C(Ph)NO_2 were prepared in Part I. β-Nitrostyrene, nitrosobenzene, *o*-nitrosotoluene, azoxybenzene, azobenzene, Dabco, PTSA, N-benzalideneaniline, *p*-nitrosodimethylaniline, *p*-nitrophenol, *p*-nitrobenzaldehyde, *p*-

nitrobenzonitrile, *p*-nitrobenzophenone, 1,4-dinitrobenzene, *p*-iodonitrobenzene, *p*-bromonitrobenzene, *o*-nitrophenylpyruvic acid, *o*-nitrocinnamaldehyde, *o*-nitrobiphenylamine, quinoline N-oxide and 2-hydroxyquinoline were purchased from Aldrich Chemical Company. Nitrobenzene was purchased from Fisher Scientific.

The following reaction products had physical and spectroscopic properties in agreement with those printed in Part I, with authentic samples or with literature values: **6a**, **6b**, **6c**, **6e** (all reported in Part I); **58** (azoxybenzene), **65** (azobenzene), **66** (N-benzylideneaniline), **73b** (N,N,N',N'-tetramethylbenzidine), **78** (N-phenyl-1,2-diphenylenediamine)(all agreement with authentic samples purchased from Aldrich Chemical Company); **44**,[14,16] isobidesyl,[15] **49**,[14,16] **60**,[17],**63**,[11,19] **64**,[11] **73a**,[18] **100**,[20] **101**,[20] **105**,[20] **106**[20] (all agreement with the appropriate literature values).

Preparation of organomercurials *tert*-butylmercury chloride

A solution containing mercuric chloride (0.18 mmol) in THF (200 mL) was stirred in an ice bath under nitrogen and *t*-BuLi (0.17 mmol, 1.7M solution in pentane) was added dropwise. After addition, the mixture was stirred overnight at room temperature. The mixture was filtered through a celite-filled sintered glass funnel and the solvent was poured into ice water solution extracted with methylene chloride. Drying with $MgSO_4$, evaporation and recrystallization to give the needle of *t*-BuHgCl: mp 110-113 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 1.51(s, 9H).

tert-Butylmercury iodide

t-BuHgCl was mixed with a two-fold excess of KI in Me_2SO and stirred 2 hours and worked up as described for the preparation of *t*-BuHgCl. The *t*-BuHgI had ^1H NMR ($CDCl_3$) δ 1.43(s, 9H).

3,3-Dimethyl-1-phenylbutene (44)[14,16]

β-Nitrostyrene (2.0 mmol), *t*-BuHgCl (4.0 mmol) and KI (10.0 mmol) were dissolved in 10 mL of Me_2SO and the mixture irradiated with a 275-W sumlamp ca. 25 cm from the reaction test tube for 19 hours. The reaction mixture was then poured into 25 mL of saturated sodium thiosulfate solution and extracted three times with 25 mL portions of methylene cholride. The combined organic extract was washed three times with saturated sodium thiosulfate and one time with brine solution. The product was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The mixture was analyzed by ^1H NMR by using toluene as internal standard to obtain compound **44** in 40% yield. The mixture was purified by flash column chromatography (silica gel, Merck, grade 60, 230-400 mesh, 60A, flash and medium-pressure liquid chromatography) with hexane to give compound **44** as a liquid. The ^1H NMR was consistent with the literature values.[14,16]

General procedure for photostimulated deoxygenation of nitroalkenes

The nitroalkene (1 mmol), *t*-BuHgI or *t*-BuHgCl (3-5 mmol) with or without Dabco or PTSA were placed in pyrex test tube and 10 mL of deoxygenated Me_2SO was added under nitrogen. With stirring the

solution was irridated with a 275-W General Electric sunlamp ca. 25 cm from the reaction test tube for 17-48 hours. The reaction mixture was then poured into 25 mL of saturated sodium thiosulfate solution, neutralized and extracted with methylene cholride. The organic extract was washed with saturated sodium thiosulfate, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The mixture was analyzed by ^1H NMR or GC by using toluene as internal standard to obtain the yields. Products were isolated by flash column chromatography with hexane:ethyl acetate = 95:5 to get the pure compounds.

O-*tert*-Butyl α-phenylacetophenone oxime (45)

Compound **45** was isolated as a solid with mp 114-117 °C and FTIR at 1603 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41-7.06(m,10H), 3.86(s, 2H), 1.31(s, 9H); ^{13}C NMR ($CDCl_3$) δ 153.4, 137.9, 133.9, 128.8, 128.6, 128.3, 127.7, 126.2, 76.4, 41.8(t), 27.5(q); GC and HRMS, m/z (relative intensity) 267.16231(M^+, 7.5, calcd for $C_{18}H_{21}NO$ 267.16236), 211(53), 193(66), 178(4), 165(5), 120(5), 103(4), 91(65), 77(12), 57(100).

Bis-*tert*-butylnitronic ester of 1,4-dinitro-1,2,3,4-tetraphenylbutane (46)

Compound **46** was isolated as solid with mp 185-186 °C; ^1H NMR ($CDCl_3$) δ 7.51-7.04(m, 16H), 6.23(d, *J*=6.9Hz, 4H), 5.20(br, 2H), 1.01(br, 18H); ^{13}C NMR ($CDCl_3$) δ 138.1, 132.7, 130.9, 129.4, 128.6,

128.3, 127.9, 127.3, 84.2, 46,6, 27.6; GCMS (CI, methane) m/z (relative intensity) 565($M+1^+$, 1.5), 406(7), 391(16), 339(7), 316(14), 298(10), 283(10), 282(6), 266(9), 238(8), 226(12), 210(33), 179(19), 105(100), 91(8). Anal. Calcd for $C_{36}H_{40}N_2O_4$: C, 76.57; H, 7.14; N, 4.96; O, 11.33. Found: C, 76.39; H, 7.22; N, 4.89.

Isobidesyl (one of the stereoisomers of 1,2,3,4-tetraphenyl-1,4-butanedione)[15]

Isobidesyl was isolated as a solid, mp 157.5-158 °C (lit.[15] mp 158-159 °C). The ^1H NMR consistent with the literature values.[15]

3-Phenylthiyl-2,2-diphenyl-2-*H*-azirine (**4b**)

Compound **4b** was isolated as a solid with FTIR at 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32-6.99(m); ^{13}C NMR ($CDCl_3$) δ 162.0, 138.6, 134.3, 129.4, 129.1, 128.9, 128.3, 127.2, 126.9, 126.8, 126.7, 126.5, 125.9, 50.6; GC and HRMS, m/z (relative intensity) 301.09235(M^+, 100, calcd for $C_{20}H_{15}NS$ 301.09260), 267(12), 223(32), 178(1), 165(9), 134(10), 77(4). The GC and GCMS are the same as 3-phenyl-2-(phenylthiyl)indole (**6b**) but solid probe MS showed a different intensity of m/z, 301(27), 267(4), 223(12), 178(4), 165(38), 134(4), 77(45).

N-*tert*-Butoxydiphenylacetamide (**47**)

Compound **47** was isolated as a solid with mp 194-197 °C and FTIR at 3294, 1643 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34-7.24(m, 10H),

5.416(br, <1H), 4.81(s, 1H), 1.32(s, 9H); ^{13}C NMR ($CDCl_3$) δ 170.9, 139.9, 128.8, 128.6, 127.0, 59.8(d), 51.5, 28.7(q); GC and HRMS, m/z (relative intensity) 283.15723(M^+, 3.3, calcd for $C_{18}H_{21}NO_2$ 283.15655), 183(19), 167(100), 152(0.3), 91(1.0), 77(1.3), 57(49). Anal. Calcd for $C_{18}H_{21}NO_2$; C, 76.30; H, 7,47; N, 4.94; O, 11.29. Found: C, 76.90; H, 7.54; N, 4.89.

α-*tert*-Butoxydiphenylacetaldehyde oxime (**48**)

Compound **48** was isolated as a solid with mp 94-94.5 °C and FTIR at 3487 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97(s, 1H), 7.38-7.20(m, 10H), 4.38(s, 1H), 1.30(s, 9H); GC and HRMS, m/z (relative intensity) 284.16478($M+1^+$, 0.2, calcd for $C_{18}H_{22}NO_2$ 284.16506), 266.15397($C_{18}H_{20}NO^+$), 227(1.8), 209(30), 192(9), 183(40), 178(82), 165(10), 152(6), 122(87), 105(64), 77(50), 57(100); GCMS (CI, ammonia), m/z (relative intensity) 301($M+NH_4^+$, 0.4), 284($M+1^+$, 86), 266(11), 217(7), 200(100), 183(30), 167(1). Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94; O, 11.29. Found: C, 75.84; H, 7.43; N,4.94.

1,1-Diphenyl-2-(N-*tert*-butoxy-N-*tert*-butylamino)propene (**50**)

Compound **50** was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 7.62-7.04(m, 10H), 1.83(s, 3H), 1.05(s, 9H); ^{13}C NMR($CDCl_3$) δ 145.0, 144.3, 142.4, 131.6, 130.2, 129.8, 128.4, 127.1, 126.1, 125.3, 77.8, 62.6, 30.9, 28.0, 17.6; GC and HRMS, m/z (relative intensity) 337.24012(M^+, 0.7, calcd for $C_{23}H_{31}NO$ 337.24056), 321(0.2), 281(22), 266(3), 234(0.9),

225(37), 208(33), 193(9), 178(7), 165(22), 105(46), 91(20), 77(17), 57(100).

Di(1-*tert*-butoxy-1,1-diphenyl-2-propylidenimino) ether (**51**)

Compound **51** was isolated as a solid, mp 169-169.5 °C with FTIR at 1599 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45-7.11(m, 20H), 1.508(s, 6H), 1.192(s, 18H); ^{13}C NMR ($CDCl_3$) δ 157.2, 143.1, 130.3, 126.791, 126.775, 86.8, 77.8, 28.0, 13.7; GC and HRMS, m/z (relative intensity) 357.20859($C_{25}H_{27}NO^+$, 1.1), 296.16510($C_{19}H_{22}NO_2^+$, 5.6), 280.16989($C_{19}H_{22}NO^+$, 21.2), 224.10709($C_{15}H_{14}NO^+$, 100), 105.03431($C_7H_5O^+$, 14). All fragments were within 2.0 ppm of the assigned atomic composition. GCMS (CI, methane), m/z (relative intensity) 617($M+C_3H_5^+$, 0.2), 605($M+C_2H_5^+$, 0.4), 577($M+H^+$, 8), 521(0.4), 394(0.9), 280(100), 224(66), 183(53), 167(11), 105(12). Anal. Calcd for $C_{38}H_{44}N_2O_3$: C, 79.13; H, 7.69; N, 4.86; O, 8.32. Found: C, 78.99; H, 7.68; N, 4.81.

General procedure for photostimulated deoxygenation of nitroso or nitro compounds

The nitroso or nitro compounds, *t*-BuHgX, KI and Dabco or PTSA were added to the pyrex test tube and then dissolved in 10 mL of Me_2SO. With stirring the solution was irradiated with a 275-W General Electric sunlamp and then worked up as previous described. The mixture was analyzed by ^1H NMR or by GC by using toluene as an internal standard, isolated by flash column chromatrography with

pure hexane followed by elute with hexane:ethyl acetate = 95:5.

N-*tert*-Butoxy-2-methyl-3-phenylindole (**52**)

A trace of **52** was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 7.64-7.05(m, 9H), 2.47(s, 3H), 1.51(s, 9H); ^{13}C NMR ($CDCl_3$) δ 136,1 135.2 134.0, 129.5, 128.4, 125.8, 123.6, 121.3, 120.1, 118.4, 111.3, 86.0, 28.3, 11.8; GC and HRMS, m/z (relative intensity) 279.16228(M^+, 26, calcd for $C_{19}H_{21}NO$ 279.16231), 223(1.2), 206(73), 194(4), 178(7), 165(9), 91(1), 77(2), 57(10).

N-(Methylsulfinylmethyloxy)-2-methyl-3-phenylindole (**53**)

A trace of compound **53** was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 7.66-7.09(m, 9H), 5.30(s, 2H), 2.55(s, 3H); ^{13}C NMR ($CDCl_3$) δ 134.7, 132.6, 131.3, 129.4, 128.5, 126.0, 123.3, 121.8, 120.5, 118.9, 110.9, 108.1, 82.2, 16.0, 10.3; HRMS, m/z (relative intensity) 283.10300(M^+, 55, calcd for $C_{17}H_{17}NOS$ 283.10309), 253(11), 238(11), 222(49), 207(51), 165(15), 61(100).

N-*tert*-Butoxy-N-*tert*-butylaniline (**62**)

Compound **62** was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 7.26-7.16(m, 3H), 7.08-7.01(m, 2H), 1.07(s, 9H), 1.05(s, 9H); ^{13}C NMR ($CDCl_3$) δ 151.1, 127.1, 126.0, 124.3, 78.0, 59.4, 28.2, 26.8; GC and HRMS, m/z (relative intensity) 221.17814(M^+, 1.0, calcd for $C_{14}H_{23}NO$ 221.17797), 165(25), 148(6), 133(2), 118(9), 109(100), 91(7), 77(16), 57(81).

N-*tert*-Butylphenylhydroxylamine (**63**)

Compound **63** was isolated as a solid, mp 113-114 °C (lit.[11] mp 115-117 °C, lit.[19] mp 116-117 °C); FTIR at 3219 cm^{-1} (lit 3220 cm^{-1}); ^1H NMR ($CDCl_3$) δ 7.23(d, *J*=4.2 Hz, 4H), 7.20(Br, 1H), 7.10(sextex, *J*=4.2 Hz, 1H), 1.085(s, 9H); ^1H NMR (d_6-DMSO) δ 8.25(s, 1H), 7.21-7.16(m, 4H), 7.04(tt, *J*=6.9, 1.5 Hz, 1H), 1.05(s, 9H); ^{13}C NMR ($CDCl_3$) δ 149.1, 127.4, 125.1, 124.6, 60.6, 25.9; GCMS, m/z (relative intensity) 165(100), 150(2), 133(4), 118(13), 109(100), 77(21), 57(69).

N-*tert*-Butylaniline (**64**)

Compound **64** was observed in GC or GCMS as a decomposition product from compound **62**; GCMS, m/z (relative intensity) 149(27), 134(100), 118(6), 91(5), 57(12).

Phenyl *tert*-butyl nitroxide [19]

The intermediate phenyl *tert*-butyl nitroxide was observed in GC and GCMS; GCMS, m/z (relative intensity) 164(4.5), 149(1), 118(4), 109(10), 108(38), 91(10), 77(19), 57(100). The nitroxide completely disappeared upon storage of the sample for two weeks.

Azoxybenzene (**58**), azobenzene (**65**), and N-benzylideneaniline (**66**)

Compounds **58**, **65**, **66** were isolated as pure compounds with ^1H NMR spectra identical to material purchased from Aldrich Chemical Company.

N-*tert*-Butoxy-N-*tert*-butyl-*o*-toluidine (**67**)

Compound **67** was isolated as a liquid; ^{1}H NMR ($CDCl_3$) δ 7.56(d, *J*=7.8 Hz, 1H), 7.12-6.98(m, 4H), 2.38(s, 3H), 1.09(s, 9H), 1.02(s, 9H); GC and HRMS, m/z (relative intensity) 235.19416(M^+, 0.7, calcd for $C_{15}H_{25}NO$ 235.19362), 179(24), 164(6), 132(7), 123(100), 106(15), 91(7), 77(4), 57(38).

N-*tert*-Butyl-*o*-toluidine (**68**)

Compound **68** was isolated as a liquid contaminated with a trace of compound **60**; ^{1}H NMR ($CDCl_3$) δ 7.53-6.63(m), 5.38(br), 2.30(s), 1.15(s); GC and HRMS, m/z (relative intensity) 163.13614(M^+, 38, calcd for $C_{11}H_{17}N$ 163.13610), 148(100), 132(6), 118(3), 107(68), 106(53), 91(10), 77(10), 57(10).

N-*tert*-Butyl-N-hydroxytoluidine (**69a**)[19]

N-*tert*-Butyl-N-hydroxytoluidine **69a** was observed in GC and GCMS, m/z (relative intensity) 179(M^+, 8), 123(100), 106(96), 91(4), 77(19), 57(28).

N-*tert*-Butyl-(2-methylphenyl)nitroxide (**69b**)[19]

Compound **69b** was isolated as a liquid. The resolution of the ^{1}H NMR spectrum was not very good but in $CDCl_3$ signals were observed at δ 7.64-6.28(m), 2.22(s), 1.41(s); GC and HRMS, m/z (relative intensity) 178.12324(M^+, 4, calcd for $C_{11}H_{16}NO$ 178.12319), 162(4), 148(15), 132(9), 122(37), 106(12), 91(16), 77(18), 57(100).

p-Dimethylamino-N-*tert*-butoxy-N-*tert*-butylaniline (**71**)

Compound **71** had ^{1}H NMR ($CDCl_3$) δ 7.13(br, 2H), 6.61(d, *J*=9.0 Hz, 2H), 2.91(s, 6H), 1.051(s, 9H), 1.046(s, 9H); GC and HRMS, m/z (relative intensity) 264.21960(M^+, 11, calcd for $C_{14}H_{28}N_2O$), 248(0.1), 217(0.3), 208(1.3), 166(100), 150(3), 136(19), 119(29), 105(16), 91(11), 77(24), 57(0.4).

p-Dimethylamino-N-*tert*-butylaniline (**72**)

Compound **72** was isolated as a liquid with FTIR: 3327 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.79(dd, *J*=8.7, 2.1 Hz, 2H), 6.65(dd, *J*=9.0, 2.1 Hz, 2H), 2.86(s, 6H), 1.19(s, 9H); GC and HRMS, m/z (relative intensity) 192.16273(M^+, 75, calcd for $C_{12}H_{20}N_2$ 192.16265), 177(62), 135(100), 121(38), 88(29), 57(6).

4,4'-Bis-dimethylaminoazoxybenzene (**73a**)[18]

Compound **73a** was isolated as a solid mp 228-232 °C (lit.[18] mp 241 °C); ^{1}H NMR ($CDCl_3$) δ 8.28(ddd, *J*=9.3, 3.3, 2.1 Hz, 2H), 8.16(ddd, *J*=9.3, 3.6, 2.1 Hz, 2H), 6.72(ddd, *J*=9.3, 3,3, 2,1 Hz, 2H), 6.68(ddd, *J*=9.3, 3.3, 2.4 Hz, 2H), 3.051(s, 6H), 3.046(s, 6H).

4,4'-Bis-dimethylaminobiphenyl (**73b**)

Compound **73b** was iolated and had an ^{1}H NMR identical with the material purchased from Aldrich Chemical Company.

p-Dimethylamino-N-*tert*-butylnitroxide (74)

Compound 74 just observed in GC and GCMS; m/z (relative intensity) 207(M^+, 8.4), 206(56), 191(54), 176(17), 149(100), 135(35), 121(10), 107(11), 95(26), 91(3), 77(10), 57(6).

2-(N-*tert*-Butoxy-N-*tert*-butylamino)diphenylamine (76)

Compound 76 was isolated as a liquid with FTIR at 3366 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.51-6.76(m, 9H), 1.13(s, 9H), 1.09(s, 9H), GC and HRMS, m/z (relative intensity) 312.22049(M^+, 23, calcd for $C_{20}H_{28}N_2O$ 312.22016), 256(40), 239(52), 199(47), 183(100). When the pure 76 was injected to the GC a decomposition peak MW=180 (phenazine) was shown.

2-(N-*tert*-Butylamino)diphenylamine (77)

Compound 77 was isolated as a liquid with FTIR at 3375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22-6.70(m, 9H), 5.31(s, 1H), 3.92(s, 1H), 1.28(s, 9H); GC and HRMS, m/z (relative intensity) 240.16278(M^+, 59, calcd for $C_{16}H_{20}N_2$ 240.162645), 225(27), 184(100), 183(63), 182(54), 169(33), 77(21), 57(25).

2-Aminodiphenylamine (78)

Isolated compound 78 was identical with an authentic sample purchased from the Alirich Chemical Company.

2-*tert*-Butylphenazine (79)

Compound **79** was isolated as a liquid;^{1}H NMR ($CDCl_3$) δ 8.26-7.81(m, 7H); 1.50(s, 9H); GC and HRMS, m/z (relative intensity) 236.13083(M^+, 35, calcd for $C_{16}H_{16}N_2$ 236.13135), 221(100), 205(16), 180(5), 77(13), 57(0.7); GCMS (CI, ammonia), m/z (relative intensity) 237($M+H^+$, 100), 221(4).

N-*tert*-Butoxy-N-*tert*-butyl-*p*-hydroxyaniline (81)

Compound **81** was isolated as a solid, mp 111-112 °C; ^{1}H NMR ($CDCl_3$) δ 7.13(br, 2H), 6.70(d, *J*=9.0 Hz, 2H), 4.86(br, 1H), 1.05(s, 9H), 1.04(s, 9H); GC and HRMS, m/z (relative intensity) 237.17254(M^+, 3.4, calcd for $C_{14}H_{23}N_2$ 237.17288), 181(29), 125(100), 108(35), 57(35).

4,4'-Azoxybenzaldehyde (83)

Compound **83** was isolated as a solid, mp 190-191 °C; ^{1}H NMR ($CDCl_3$) δ 10.2(s, 1H), 10.1(s, 1H), 8.51(d, *J*=8.7 Hz, 2H), 8.28(d, *J*=8.7 Hz, 2H), 8.07(dd, *J*=8.7, 1.5 Hz, 2H), 8.02(dd, *J*=8.4, 1.5 Hz, 2H); GC and HRMS, m/z (relative intensity) 254.06860(M^+, 19, calcd for $C_{14}H_{10}N_2O_3$ 254.06914), 226(3), 169(3), 133(20), 119(5), 115(3), 105(100), 77(43).

p-(N-*tert*-Butoxy-N-*tert*-butylamino)benzaldehyde (84)

Compound **84** was isolated as a solid mp 40-45 °C; ^{1}H NMR ($CDCl_3$) δ 9.93(s, 1H), 7.76(dd, *J*=9.0, 1.5 Hz, 2H), 7.42(br, 2H), 1.12(s, 9H), 1.07(s, 9H); GC and HRMS, m/z (relative intensity) 249.17287(M^+,

0.9, calcd for $C_{15}H_{23}NO_2$ 249.17288), 193((20), 137(100), 91(3), 77(5), 57(69).

N-*tert*-Butyl-4,4'-dicyanohydrazobenzene (**86**)

Compound **86** was isolated as solid, mp 62-65 °C with FTIR at 3312, 2250, 2214 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.52(d, *J*=8.7 Hz, 2H), 7.41(d, *J*=8.7 Hz, 2H), 7.27(d, *J*=8.7 Hz, 2H), 6.89(d, *J*=8.7 Hz, 2H), 6.68(s, 1H), 1.32(s, 9H); ^{13}C NMR ($CDCl_3$) δ 152.0, 151.7, 133.6, 132.4, 132.2, 120.2, 119.0, 111.5, 106.0, 100.1, 60.6, 27.3; GC and HRMS, m/z (relative intensity) 290.15294(M^+, 13, calcd for $C_{18}H_{18}N_4$ 190.15315), 234(100), 207(2), 143(5), 117(8), 102(21), 57(60).

p-(N-*tert*-Butoxy-N-*tert*-butylamino)benzonitrile (**87**)

Compound **87** was isolated as a liquid with FTIR at 2226 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.52(d, *J*=8.7 Hz, 2H), 7.38(br, 2H), 1.09(s, 9H), 1.05(s, 9H); GC and HRMS, m/z (relative intensity) 246.17321(M^+, 0.3, calcd for $C_{15}H_{25}N_2O$ 246.17321), 190(22), 173(10), 143(9), 134(77), 102(8), 75(2), 57(100).

N-*tert*-Butyl-*p*-cyanophenylhydroxyamine (**88**)

Compound **88** was isolated as a liquid with a purity of about 82% by GC, the sample had an FTIR at 3381, 2212 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36(dd, *J*=8.7, 1.8 Hz, 2H), 6.60(dd, *J*=9.0, 1.8 Hz, 2H), 4.18(br, 1H), 1.38(s, 9H); GC and HRMS, m/z (relative intensity) 190.11050(M^+, 31, calcd for $C_{11}H_{14}N_2O$ 190.11062), 174(19), 159(50), 143(11), 134(92),

118(49), 102(11).

4,4'-Azoxydibenzophenone (**20**)

Compound **20** was isolated as a solid, mp 198.5-199.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.16(dd, *J*=9.0, 1.8 Hz, 2H), 8.26(dd, *J*=8.4, 1.8 Hz, 2H), 7.98-7.18(m, 14H); ^{13}C NMR ($CDCl_3$) δ 217.3, 217.0, 195.5, 195.2, 150.2, 146.5, 140.6, 138.0, 137.2, 136.7, 133.1, 132.6, 130.6, 130.0, 128.5, 128.4, 127,3, 122.5; GC and HRMS, m/z (relative intensity) 406,13201(M^+, 65, calcd for $C_{26}H_{18}N_2O_3$ 406.13174), 390(6), 197(10), 181(46), 153(15), 105(100), 77(30).

p-(N-*tert*-Butoxy-N-*tert*-butylamino)benzophenone (**21**)

Compound **21** was isolated had ^{1}H NMR ($CDCl_3$) δ 7.81-7.38(m, 9H), 1.13(s, 9H), 1.08(s, 9H); ^{13}C NMR ($CDCl_3$) δ 196.0, 156.8, 138.1, 133.4, 131.9, 129.8, 129.7, 128.1, 125.3, 78.7, 60.1, 28.1, 26.9; GC and HRMS, m/z (relative intensity) 326.21137($M+1^+$, 2, calcd for $C_{21}H_{28}NO_2$ 326.21200), 325.20524($C_{21}H_{27}NO_2^+$, 0.5), 269(15), 252(3), 238(2), 213(100), 182(1), 136(13), 105(24), 77(15), 57(64); GCMS (CI, ammonia), m/z (relative intensity) 343($M+NH_4^+$, 19), 326($M+H^+$, 100), 254(22).

p-(N-*tert*-Butylamino)benzophenone (**22**)

Compound **22** was as solid, mp 126-130 °C; FTIR at 3427, 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.77-7.31(m, 9H), 6.63(br, 1H), 1.17(s, 9H); GC and HRMS, m/z (relative intensity) 253.14704(M^+, 13, calcd for

$C_{17}H_{19}NO$ 253.14666), 238(79), 197(21), 120(100), 105(50), 92(12), 77(37), 57(26).

Tri-*tert*-butylphenylhydroxylamine (**95**)

Compound **95** was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 7.20-7.13(m, 4H), 1.29(s, 9H), 1.07(s, 9H), 1.04(s, 9H); GC and HRMS, m/z (relative intensity) 277.24005(M^+, 1.1, calcd for $C_{18}H_{31}NO$ 277.24056), 221(22), 165(100), 150(71), 91(3), 77(2), 57(39).

O-(Methylsulfinylmethyl)-*p*-nitrophenol (**96**)

Compound **96** was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 8.21(d, *J*=9.3 Hz, 2H), 7.02(d, *J*=9.3 Hz, 2H), 5.24(s, 2H), 2.28(s, 3H); GC and HRMS, m/z (relative intensity) 199.02990(M^+, 2.6, calcd for $C_8H_9NO_3S$ 199.03032), 76(3), 61(100).

p-Nitro-N-*tert*-butylaniline (**97**)

Compound **97** was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 8.04(ddd, *J*=9.0, 3.6, 1.5 Hz, 2H), 6.60(ddd, *J*=9.3, 3.3, 1.5 Hz, 2H), 4.57(br, 1H), 1.44(s, 9H); GC and HRMS, m/z (relative intensity) 194.10552(M^+, 27, calcd for $C_{10}H_{14}N_2O_2$ 194.10553), 179(100), 138(38), 108(19), 92(17), 91(6), 77(4), 57(72).

p-Iodo-N-*tert*-butoxy-N-butylaniline (**99**)

Compound **99** was isolated as a solid, mp 211-213 °C; ^1H NMR ($CDCl_3$) δ 7.52(d, *J*=8.7 Hz, 2H), 7.02(br, 2H), 1.06(s, 9H), 1.04(s, 9H); GC

and HRMS, m/z (relative intensity) 347.07411(M^+,0.6, calcd for $C_{14}H_{22}INO$ 347.07462), 291(16), 235((17), 218(5), 127(0.1), 108(4), 91(2), 77(2), 76(7), 57(100).

N-*tert*-Butyl-*p*-iodophenylhydroxylamine(**100**)[20]

Compound **100** was isolated as a solid, mp 119-120 °C with FTIR at 3381 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53(d, *J*=8.4 Hz, 2H), 6.95(d, *J*=8.7 Hz, 2H), 1.08(s, 9H); GC and HRMS, m/z (relative intensity) 291.01137(M^+, 17, calcd for $C_{10}H_{14}INO$ 291.01202), 275(49), 260(100), 235(95), 218(30), 127(8), 57(90); GCMS (CI, methane), m/z (relative intensity) 309($M+NH_4^+$, 27), 292($M+H^+$), 276(100), 166(14), 150(14).

p-Iodo-N-*tert*-butylaniline (**101**)[20]

Compound **101** was isolated as a liquid with FTIR at 3410 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38(d, *J*=8.4 Hz, 2H), 6.50(d, *J*=8.7 Hz, 2H), 3.28(br, 1H), 1.32(s, 9H); GC and HRMS, m/z (relative intensity) 275.01667(M^+, 54, calcd for $C_{10}H_{14}IN$ 275.01710), 260(94), 244(3), 219(100), 148(4), 77(5), 57(49).

p-Bromo-N-*tert*-butoxy-N-*tert*-butylaniline (**104**)

Compound **104** was isolated as a solid, mp 38-39 °C; ^1H NMR ($CDCl_3$) δ 7.32(dd, *J*=9.0, 1.2 Hz, 2H), 7.15(br, 2H), 1.06(s, 9H), 1.04(s, 9H); GC and HRMS, m/z (relative intensity) 299.08812(M^+, 0.6, calcd for $C_{14}H_{22}BrNO$ 299.08848), 245(8), 243(10), 228(3), 226(2),

189(41), 187(39), 108(2), 91(2), 77(1), 57(100).

p-Bromo-N-*tert*-butylphenylhydroxylamine (**105**)[20]

Compound **105** was isolated as a solid, mp 130-132 °C with FTIR at 3209 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34(dd, *J*=9.0, 2.1 Hz, 2H), 7.09(dd, *J*=8.7, 2.7 Hz, 2H), 6.61(br, 1H), 1.09(s, 9H). The pure compound decomposed under GC condition to give **106**.

p-Bromo-N-*tert*-butylaniline (**106**)[20]

Compound **106** was isolated as a liquid with FTIR at 3406 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22(ddd, *J*=9.0, 3.0, 2.4 Hz, 2H), 6.60(ddd, *J*=8.7, 3.3, 2.1 Hz, 2H), 3.33(br, 1H), 1.32(s, 9H); GC and HRMS, m/z (relative intensity) 229(29), 227.03802(M^+, 31, calcd for $C_{10}H_{14}Br$ 227.03096), 214(74), 212(76), 173(94), 171(100), 132(26), 107(12), 106(12), 92(33), 91(13), 77(5), 57(45).

N-*tert*-Butoxyoxindole (**108**)

Compound **108** was isolated as a liquid with FTIR at 1744 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29-6.98(m, 4H), 3.51(s, 2H), 1.45(s, 9H); GC and HRMS, m/z (relative intensity) 205.11075(M^+, 4, calcd for $C_{12}H_{15}NO_2$ 205.11028), 149(100), 132(59), 121(24), 104(8), 93(54), 77(14), 57(35).

2,3-Di-*tert*-butyl-4-hydroxy-3,4-dihydroquinoline (**109a**)

Compound **109a** was isolated as a solid, mp 124-125 °C with

FTIR at 3281, 1614 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42-7.16(m, 4H), 4.52(dd, *J*=9.3, 1.2 Hz, 1H), 2.68(d, *J*=1.2 Hz, 1H), 1.65(d, *J*=9.6 Hz, 1H), 1.35(s, 9H), 0.88(s, 9H); ^1H NMR ($CDCl_3$ plus D_2O) δ 4.51(s), 2.67(s), 1.65(no absorption); ^{13}C NMR ($CDCl_3$) δ 176.8(s), 143.6(s), 131.8(d), 127.8(d), 127.1(d), 126.1(d), 125.1(s), 61.3(d), 54.5(d), 39.2(s), 33.9(s), 28.6(q), 28.0(q); GC and HRMS, m/z (relative intensity) 259.19287(M^+, 40, calcd for $C_{17}H_{25}NO$ 259.19361), 244(96), 217(5), 202(31), 186(100), 170(28), 146(54), 118(21), 91(9), 77(3), 57(48); GCMS (CI, ammonia) m/z (relative intensity) 260($M+1^+$, 100), 186(3), Anal. Calcd. for $C_{17}H_{25}NO$: C, 78.72; H, 9.71; N, 5.40; O, 6.17. Found: C, 78.36; H, 9.45; N, 5.33.

3,4-Di-*tert*-butyl-3,4-dihydro-2-quinolinone (**109c**)

Compound **109c** was isolated as solid, mp 144-147 °C with FTIR at 3204, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.34(br, 1H), 7.17-6.77(m, 4H), 2.72(s, 1H), 2.60(s, 1H), 0.92(s, 9H), 0.88(s, 9H); GC and HRMS, m/z (relative intensity) 259.19372(M+, 4.4, calcd for $C_{17}H_{25}NO$ 259.19361), 201(29), 186(32), 167(14), 159(65), 146(100), 117(8), 57(13).

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PART III. PROMOTION OF ELECTRON TRANSFER BY PROTONATION OF NITROGEN-CENTERED FREE RADICALS

Promotion of electron transfer by protonation of nitrogen-centered free radicals

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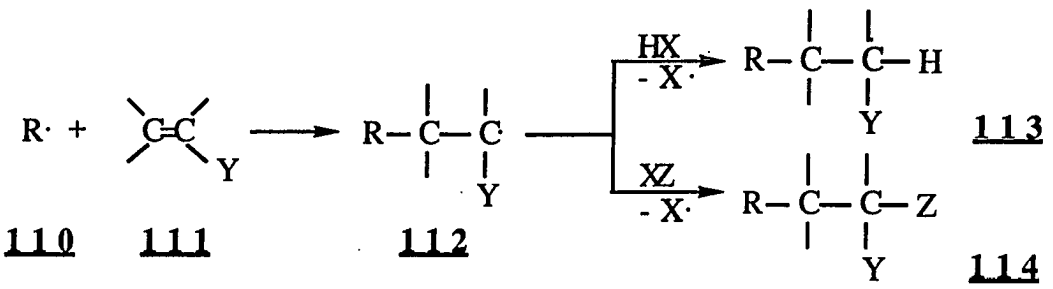
ABSTRACT

Photostimulated reactions of organomercurials with electron deficient cyano-substituted olefins in the presence of PTSA (*p*-toluenesulfonic acid) or Dabco (1,4-diazabicyclo[2.2.2]octane) leads to the reductive alkylation of mono- and di-functional α,β-unsaturated nitriles. The yields obtained depend upon a number of factors, e.g. the mole ratios of the reactants, acidic or basic conditions and the presence of a reducing agent such as I^-. *tert*-Butyl radicals react with cyano olefins or alkylidene malononitriles to form monoalkylated products in the presence of PTSA or Dabco. Fumaronitrile reacts with *tert*-butyl or isopropyl radicals to form the saturated dinitrile products in the presence of PTSA and to form mono- or dialkylated butenedinitriles in the presence of Dabco. Addition of *tert*-butyl radical to 2-(1-alkenyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazines leads to high yields of the alkylated oxazines in the presence of proton donors and iodide ion.

INTRODUCTION

The most important methodology for the synthesis of aliphatic C-C bonds via radical reactions is the addition of alkyl radicals to alkenes **111**. This reaction leads to adduct radical **112** that must be converted to non-radical products before polymerization occurs. Polymerization is avoided either by intermolecular trapping of the adduct radical **112** or by intramolecular homolytic bond cleavage. Hydrogen atom donors X-H or heteroatom donors X-Z are used as trapping agents.

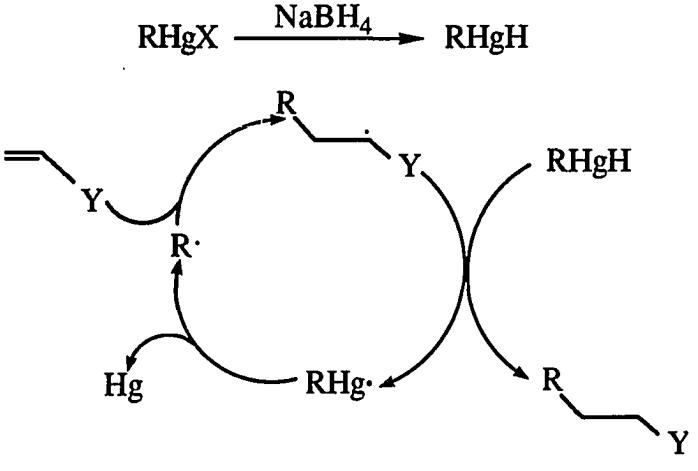


110 **111** **112** **113** **114**

In this competition system, alkyl radical **110** must react faster with the alkene than with HX or XZ and adduct the radical **112** must react faster with the radical trap than with the alkene. If this is not the case, either radicals are trapped before they can form a C-C bond or the adduct radicals react with the alkene to give polymers. This selectivity requirement can be fulfilled by choosing suitably substituted alkenes. With nucleophilic alkyl radicals **110** one has to use alkenes **111** with electron-withdrawing groups Y that reduce the

nucleophilic character of the adduct radicals **112**. Normally, at least a ten-fold excess of an olefin with an electron withdrawing substitute is needed for good yields.

The reduction of alkylmercury salts with hydrogen donors like $NaBH_4$ or Bu_3SnH leads to alkylmercury hydrides that trap alkyl radicals to form product. Reactive alkenes like acrylonitrile, vinyl ketones, arylates, fumarodinitrile, or maleic anhydrides[1,2] react with alkyl radicals in the presence of $NaBH_4$ to form high yields of products.



Russell et.al. has reported that chain reactions between alkylmercury halides and some deficient alkenes [CH_2=CH(EWG)] involving Eq. 1, e.g. with EWG = $PhSO_2$ or $(EtO)_2P(O)$.[3]

$$R\cdot + CH_2{=}CH(EWG) \longrightarrow RCH_2\dot{C}H(EWG) \xrightarrow{RHgCl}$$

$$R\cdot + RCH_2CH(HgCl)EWG \xrightarrow{NaBH_4} RCH_2CH_2(EWG) + Hg^{\circ} \quad (1)$$

Although α,β-unsaturated carbonyl compounds react inefficiently with RHgCl when photostimulated, reactions occur readily in the presence of iodide ion in Me_2SO by virtue of electron transfer between the adduct enolyl radical and $RHgI_2^-$, Eq. 2.[4,5] However, adduct radicals from α,β-unsaturated nitriles do not undergo this reaction efficiently.

$$RCH_2\dot{C}HC(O)Y + RHgI_2^- \longrightarrow RCH_2CH{=}C(O^-)Y + R\cdot + HgI_2 \quad (2)$$

We have found that intermediate adduct radicals such as,

$$RCH(R')\dot{C}(Y)C{\equiv}N \longleftrightarrow RCH(R')C(Y){=}C{=}\dot{N}$$

or

$$RCH_2\dot{C}(R')C(Y){=}NR^2 \longleftrightarrow RCH_2C(R'){=}C(Y)\dot{N}R^2$$

although often unreactive in reactions 1 or 2, will undergo chain propagation reactions with $RHgI/I^-$ in the presence of proton donors such as PTSA, Eq. 3,4.[6] In the

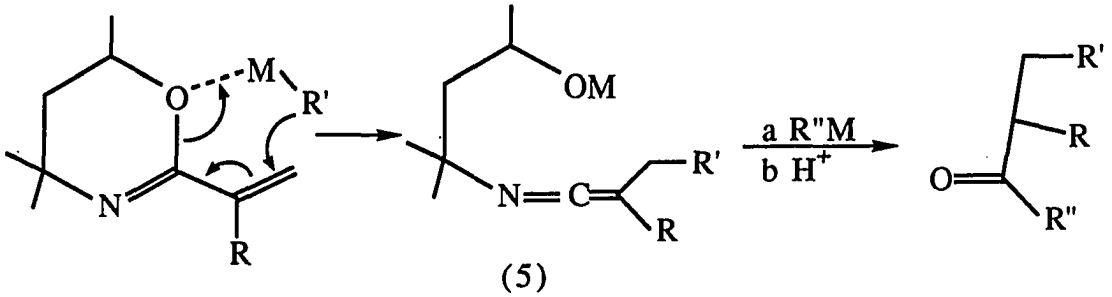
$$\}{=}C{=}NH^{+\cdot} + RHgI_2^- \xrightarrow{Me_2SO} \}{=}C{=}NH + R\cdot + HgI_2 \quad (3)$$

$$\}{=}C(Y)NH(R')^{+\cdot} + RHgI_2^- \xrightarrow{Me_2SO} \}{=}C(Y)NH(R') + R\cdot + HgI_2 \quad (4)$$

absence of a proton donor, dimerization products are often the major products observed for vinylaminyl radicals. Thus, for *t*-BuCH2CH(CN)· the proton donor decrease the yield of the dimerization or oligomerization products and increases the yield of *t*-BuCH2CH2CN/*t*-

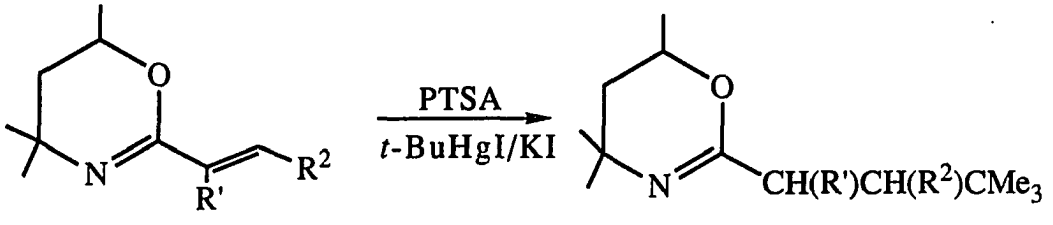
$BuCH_2CH_2CONH_2$. In Me_2SO(1)-EtOH(1) solvent system the production of the ester suggests that the ketenimine is an intermediate for the reaction in the presence of PTSA.

Addition of organolithium and Grignard reagents to 2-alkenyloxazines leads to alkylation via the ketenimine intermediate, Eq. 5.[7] React of tert-butyl



(5)

radicals with 2-isopropenyl, 2-(α-styryl) and 2-(β-styryl)oxazines in the presence of KI and PTSA all form high yields of the oxazines, Eq. 6.



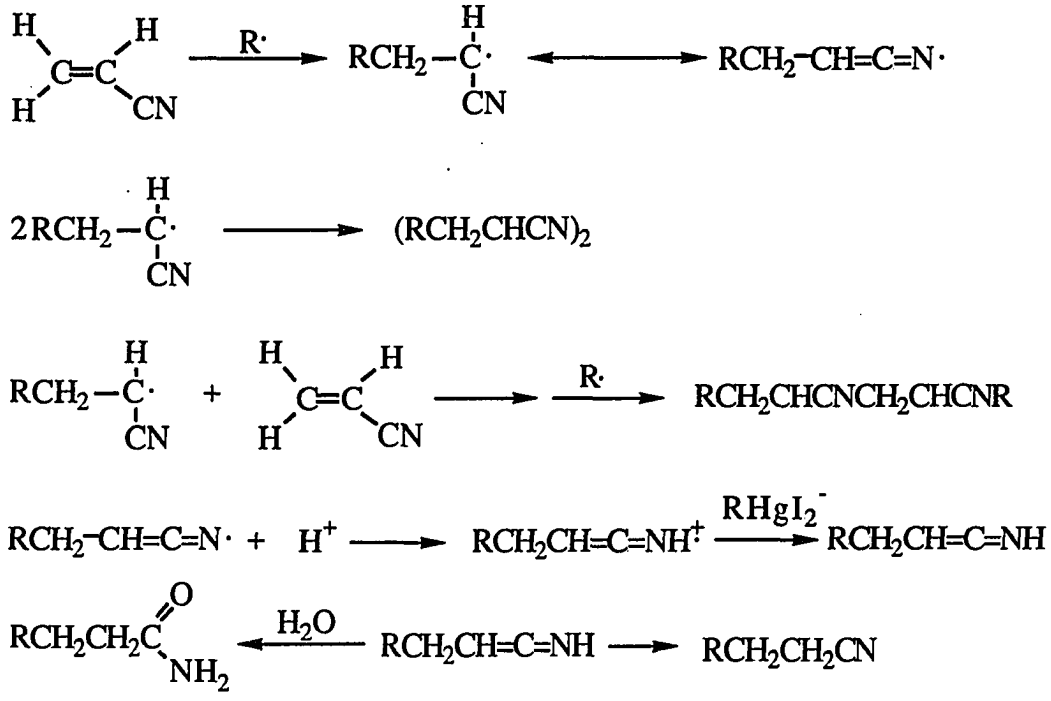
(6)

RESULTS AND DISCUSSION

Reactions of *tert*-butyl radicals with acrylonitrile

Acrylonitrile reacted slowly upon photolysis in the presence of *t*-BuHgI/KI to form the dimer or oligomer (Scheme I). However, in the presence of Dabco, or better in the presence of PTSA, the *tert*-butylated nitriles and amide were the major products (Table 1). The presumed mechanism in the presence of a proton donor is shown in Scheme I. In Me_2SO(1)-EtOH(1) the ketenimine can be trapped by

Scheme I



EtOH to form ethyl 4,4-dimethyl-pentanoate (>18%).

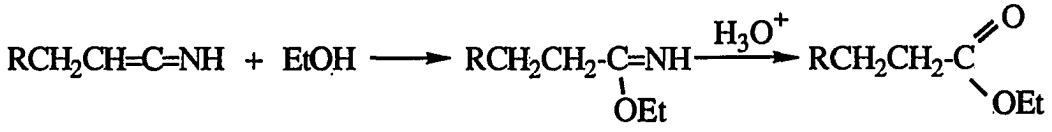
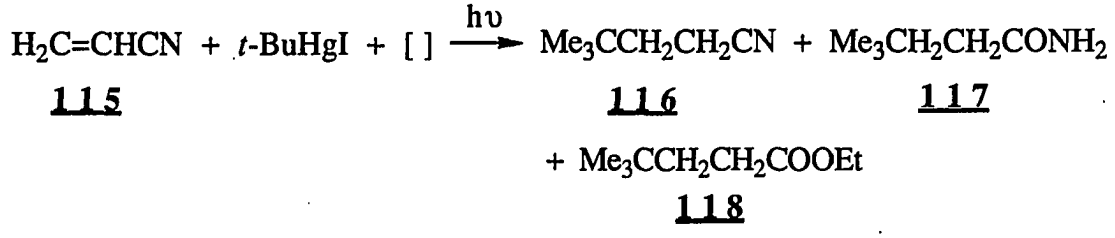


Table 1. Alkylation of acrylonitrile by *t*-BuHgI in Me_2SO[a]



Molar equivalents			Time (h)	% Yield[b]		
t-BuHgI:	KI:	D or P[c]		**116**	**117**	**118**
3 :	3 :	0	23	tr	tr	-
2 :	4 :	2 (D)	48	30	tr	-
3 :	3 :	3 (P)	23	33	24	-
5 :	5 :	5 (P)	23	40	35	-
2 :	2 :	0	48	33[d]	15[d]	-
5 :	5 :	5 (P)	24	13[e]	13[e]	>18

[a] 0.05-0.2 M of acrylonitrile in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

Table 1. (continued)

[c] (D) means Dabco and (P) means PTSA, which are the chemical for "[ ]" in the reaction.

[d] 0.2 M of Acrylonitrile in 10 mL of Me2SO and 0.5 mL of HI (aq).

[e] 0.1 M of Acrylonitrile in 5 mL of Me2SO and 5 mL of EtOH.

Reaction of *tert*-butyl radicals with crotononitrile (cis/trans mixture)

The reaction of crotononitrile (cis/trans mixture) with *tert*-butyl radical in the presence of PTSA gave results similar to those observed for acrylonitrile. The alkylated nitrile **120** and amide **121** were formed in high yield (72%) in the presence of PTSA while in the absence of PTSA the saturated nitrile was formed in less than 16% yield. Giese observed the reaction of cyclohexyl radical with (*E*) or (Z) -crotononitrile in the presence of NaBH4 to form the saturated adduct in a low yield from 33-37%.

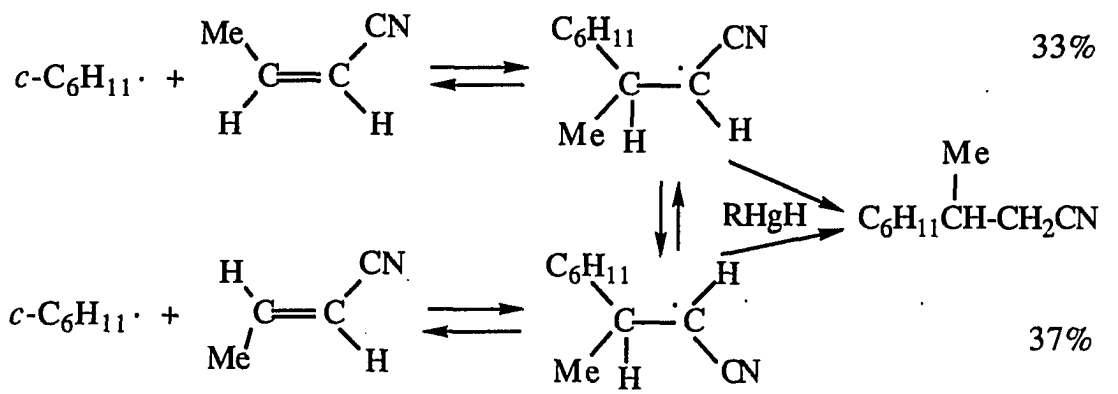


Table 2. Photostimulated reactions of *t*-BuHgI with crotononitrile (*E*, *Z*- mixture) in Me_2SO[a]

$$MeCH{=}CHCN + t\text{-}BuHgI + [\,] \xrightarrow{h\upsilon} Me_3CCHMeCH_2CN + Me_3CCHMeCH_2CONH_2$$

119 **120** **121**

Molar equivalents			Time (h)	% Yield[b]	
t-BuHgI:	KI:	PTSA[c]		**120**	**121**
2 :	2 :	0	23	16	-
2 :	2 :	3	23	60	12

[a] 0.05-0.2 M of crotononitrile in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

[c] PTSA is the chemical for "[ ]" in the reaction.

Reaction of *tert*-butyl radicals with α-chloroacrylonitrile

The reaction of cyclohexyl radical and *tert*-butyl radical with α-chloroacrylonitrile have been reported by Giese using $NaBH_4$.[8] The yields are 48% with the former radical and 52% with the latter. With PTSA the major products were 2-chloro-4,4-dimethyl-pentanenitrile in 65% yield and 13% of 4,5-dicyano-2,2,7,7-tetramethyl-4-octene (Table 3). For this nitrile the presence of Dabco did not increase the yield of the alkylated nitrile.

Table 3. Photostimulated reactions of *t*-BuHgI with α-chloroacrylonitrile in Me_2SO[a]

$$H_2C{=}C(CN)Cl + t\text{-BuHgI} + [\,] \xrightarrow{h\upsilon} Me_3CCH_2CH(CN)Cl + [Me_3CCH_2(CN)C]_2$$

122 **123** **124**

Molar equivalents			Time (h)	% Yield[b]	
t-BuHgI:	KI:	(D) or (P)[c]		**123**	**124**
5 :	5 :	0	23	20	-
2 :	4 :	2 (D)	47	12	-
5 :	5 :	5 (P)	36	65	13

[a] 0.05-0.2 M of α-chloroacrylonitrile in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

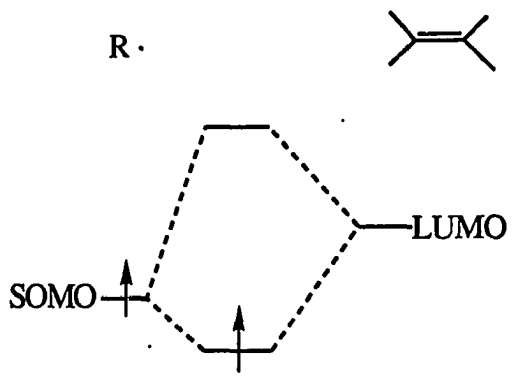
[b] By NMR with toluene as an internal standard.

[c] (D) means Dabco and (P) means PTSA, which are the chemical for "[ ]" in the reaction.

Reaction of *tert*-butyl radicals with ethyl trans-α-cyanocinnamate, α-phenylcinnamonitrile and methacrylonitrile

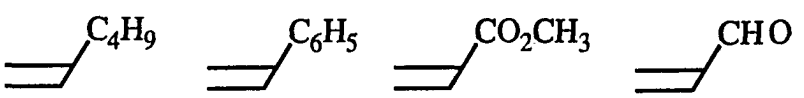
The rate of addition of a radical to an alkene depends upon the substituents on the radical and alkene. These substituent effects can be described by FMO theory.[9] The singly occupied orbital (SOMO) of the radical interacts with the lowest unoccupied orbital (LUMO) and/or the highest occupied orbital (HOMO) of the CC-multiple bond.

Radicals with a high lying SOMO interact preferentially with the LUMO of the alkene.



Orbital interaction between a nucleophilic radical and on electron-poor alkene

Electron withdrawing substituents on the alkene, which lower the LUMO energy, increase the rate of addition by reducing the SOMO-LUMO energy gap. Some representive relative reactivity data determined by Giese in competitive reactions with *c*-$C_6H_{11}HgCl/NaBH_4$ are given below.

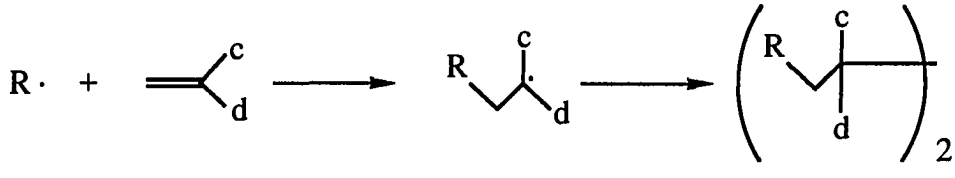


1.0 84 3000 8500

Comparing methacrylonitrile to α-phenylcinnamonitrile and ethyl trans-α-cyanocinnamate, the alkyl group is electron-donating while the ester group is electron-withdrawing. The phenyl group may

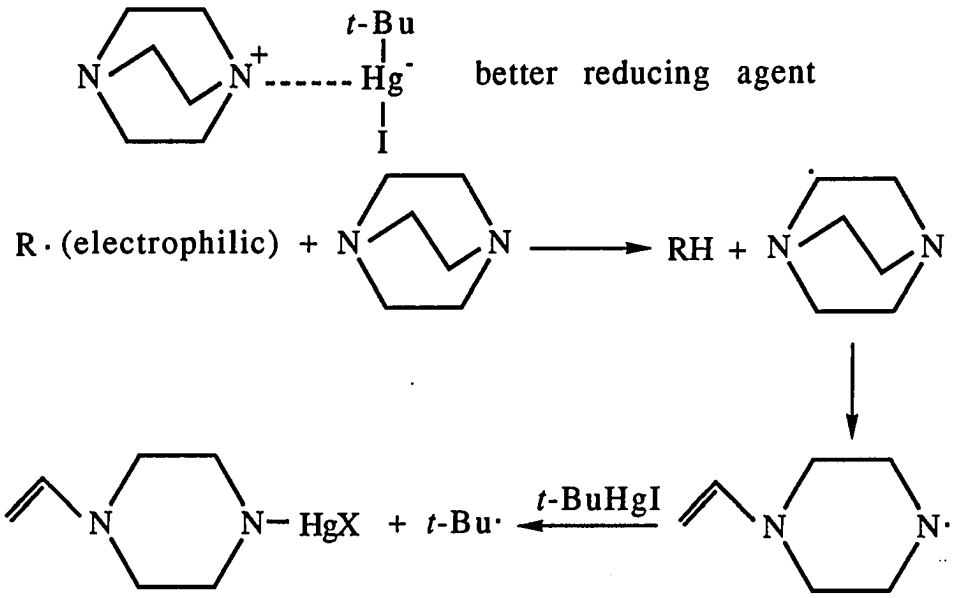
also play an important role in stabilizing the adduct radical. The ethyl trans-α-cyanocinnamate gives high yields of monoalkylated with *t*-BuHgCl/KI in the presence of acid or base (Table 4). Methacrylonitrile forms monoalkylated product (60%) together with the dimer or oligomer (25%) in the presence of Dabco while dimers or oligomer (60%) are the major products in the presence of PTSA (Table 5).

One possibility is that methacrylonitrile forms a capto-dative stabilized radical which is not reduced by *t*-$BuHgI_2^-$ even in the presence of PTSA. With Dabco the monoalkylation product increases from 30% to 60% and the dimers or oligomers decrease from 46% to 25% (Table 5) when the ratio of *t*-BuHgI and Dabco to methacrylonitrile increase from 2 to 5 equivalents. Possibly the Dabco can form a complex with *t*-BuHgI which is a better reducing agent than *t*-$BuHgI_2^-$ or maybe the Dabco is a hydrogen atom donor to the electrophilic adduct radical.



c: capto (electron-withdrawing) substituent

d: dative (electron-releasing) substituent



Reaction of α-phenylcinnamonitrile with *t*-butyl radical forms an adduct radical which is benzylic radical and reasonably persistent. The benzylic radical can trap another *tert*-butyl radical particularly when protonated to form the ketenimine radical cation and when the ratio of *t*-BuHgI/PhCH=C(Ph)CN is higher. The possible reaction pathways in the presence of PTSA are shown in Scheme II.

Scheme II

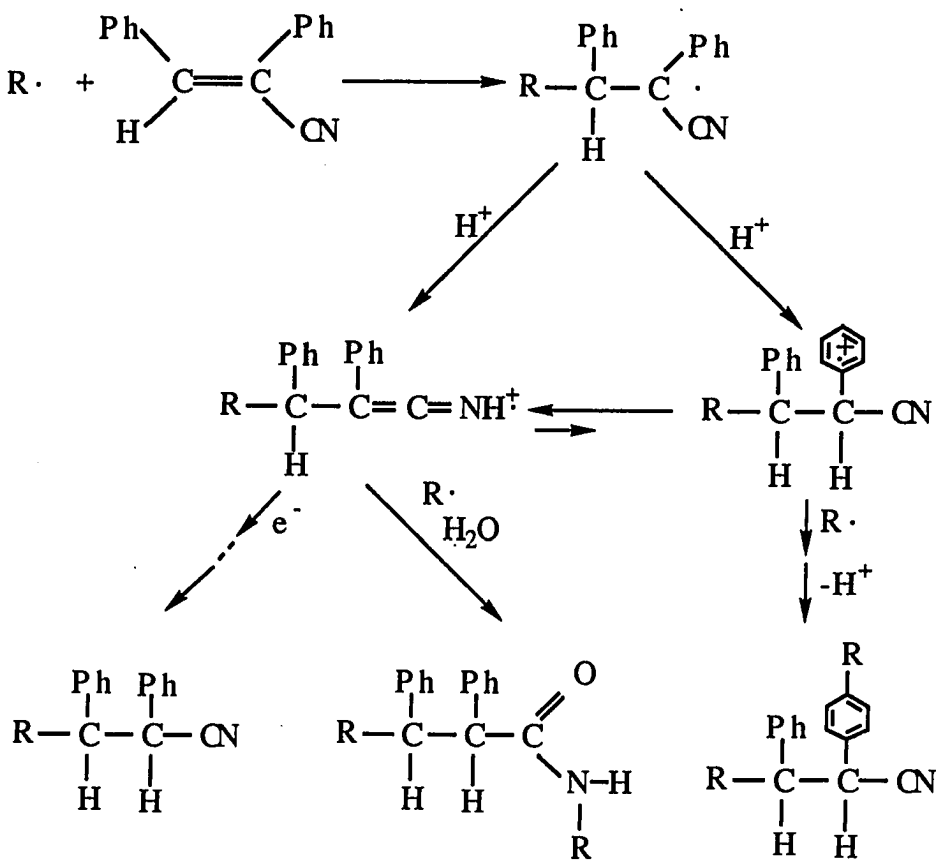


Table 4. Photostimulated reactions of *t*-BuHgI with ethyl (*E*)-α-cyanocinnamate in Me_2SO[a]

$$PhCH{=}C(CN)COOEt + t\text{-}BuHgI + [\,] \xrightarrow{h\upsilon} Me_3CCHPhCCN(COOEt)H$$

125 **126**

Molar equivalents			Time (h)	% Yield[b]
t-BuHgI:	KI:	(D) or (P)[c]		**126**
2 :	4 :	2 (D)	22	77[d]
4 :	4 :	4 (P)	22	83

[a] 0.05-0.2 M of ethyl (*E*)-α-cyanocinnamate in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

[c] (D) means Dabco and (P) means PTSA, which are the chemical for "[ ]" in the reaction.

[d] Mixture of diastereomers.

Table 5. Photostimulated reactions of *t*-BuHgI with methacrylonitrile in Me_2SO[a]

$$H_2C{=}CMeCN + t\text{-BuHgI} + [\,] \xrightarrow{h\upsilon} Me_3CCH_2CH(Me)CN + [Me_3CCH_2C(Me)CN]_2$$

127 **128** **129**

Molar equivalents			Time (h)	% Yield[b]	
t-BuHgI:	KI:	(D) or (P)[c]		**128**	**129**
2 :	4 :	0	47	30	46
5 :	5 :	5 (D)	20	60	25
3 :	3 :	3 (P)	23	tr	50
5 :	5 :	3 (P)	19	tr	60[d]

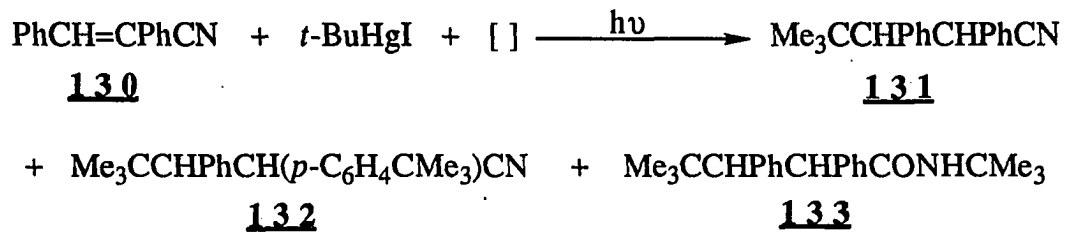
[a] 0.1-0.2 M of methacrylonitrile in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

[c] (D) means Dabco and (P) means PTSA, which are the chemical for "[ ]" in the reaction.

[d] Including the amide products.

Table 6. Photostimulated reactions of *t*-BuHgI with α-phenylcinnamonitrile in Me_2SO[a]



Molar equivalents			Time (h)	% Yield[b]		
t-BuHgI:	KI:	(D) or (P)[c]		131	132	133
2 :	4 :	0	96	46[d]	tr	tr[e]
2 :	4 :	2 (D)	96	31[d]	tr	tr[e]
5 :	5 :	5 (P)	36	~50	~20[f]	~20[f]

[a] 0.1 M of α-phenylcinnamonitrile in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

[c] (D) means Dabco and (P) means PTSA, which are the chemical for "[ ]" in the reaction.

[d] Mixture of diastereomers.

[e] Unreacted α-phenylcinnamonitrile remained at the end of the reaction.

[f] Mixture of diastereomers.

Reactions of *tert*-butyl radical with alkylidenemalononitriles and benzylidenemalononitrile

Intermolecular trapping of alkyl radicals with electron deficient alkenes containing an α-alkyl substituent (e.g. Me group) is not a particularly useful synthetic reaction from the above results and from Giese's report.[8] In the case of β-Me group, the rate retarding effect (or reversibilty of a radical addition to an olefin) can be counterbalanced by placing two cyano groups in a geminal position of the alkene.[10] This concept has been utilized for the preparation of alkanoic acids by coupling alkylidenemalononitriles with alkyl radicals generated from the alkylmercuric chlorides and $NaBH_4$, followed by hydrolysis and decarboxylation. The required cyano olefins have been prepared by the Knoevengel reaction of aldehyde or ketones with malononitrile.

$$R^1CHO + CH_2(CN)CN \longrightarrow R^1CH{=}C(CN)CN \xrightarrow[NaBH_4]{R^2HgCl} R^1R^2CH\text{-}CH(CN)CN \longrightarrow R^1R^2CHCH_2COOH$$

Similar results have been observed in reactions α,β-unsaturated dinitriles such as benzylidenemalononitrile or isopropylidenemalononitrile with *tert*-butyl or benzyl radicals in the presence of PTSA. The mechanism is shown in Scheme III. The results are given in Tables 7-9.

Scheme III

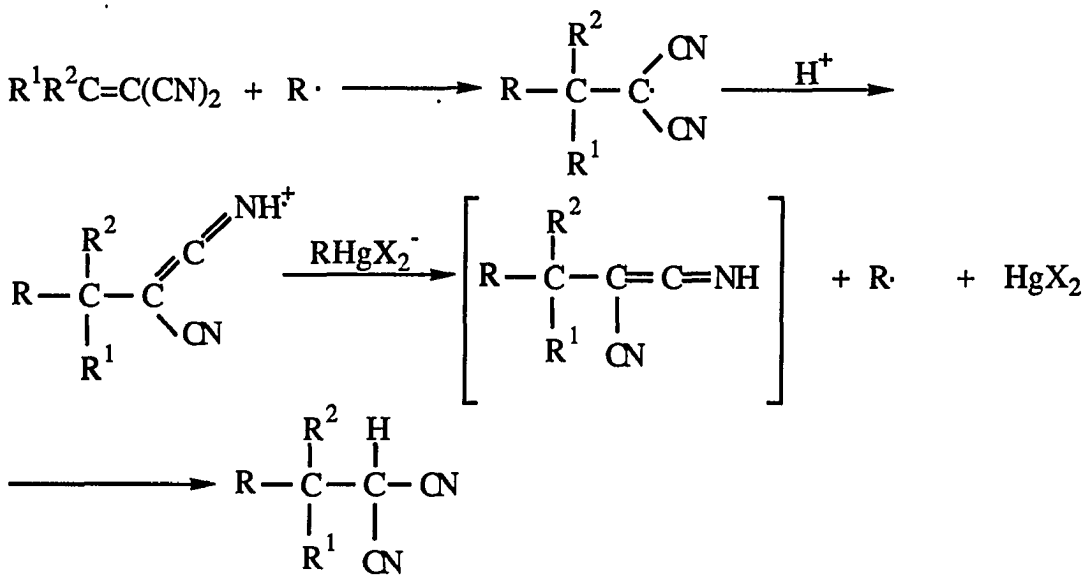


Table 7. Photostimulated reactions of *t*-BuHgI with benzylidenemalononitrile in Me_2SO[a]

$$PhCH{=}C(CN)_2 + t\text{-BuHgI} + [\ ] \xrightarrow{h\upsilon} Me_3CCH(Ph)CH(CN)_2 + Me_3CC(Ph){=}C(CN)_2$$

134 **135** **136**

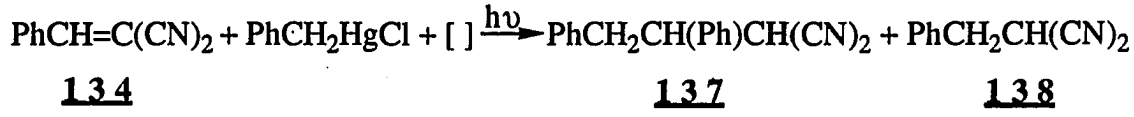
Molar equivalents			Time (h)	% Yield[b]	
t-BuHgI:	KI:	(D) or (P)[c]		**135**	**136**
2 :	4 :	0	17	41	-
2 :	4 :	2 (D)	47	70	6
2 :	4 :	4 (P)	23	91	-
4 :	4 :	4 (P)	22	99	-

[a] 0.05-0.2 M of $PhCH{=}C(CN)_2$ in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

[c] (D) means Dabco and (P) means PTSA, which are the chemical for "[ ]" in the reaction.

Table 8. Photostimulated reactions of $PhCH_2HgCl$ with benzylidenemalononitrile in Me_2SO[a]



134 **137** **138**

Molar equivalents			Time (h)	% Yield[b]	
t-BuHgI:	KI:	Dabco[c]		**137**	**138**
2 :	0 :	2	72	50	-
2 :	4 :	2	33	~50	~33

[a] 0.2 M of $PhCH=C(CN)_2$ in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

[c] Dabco is the chemical for "[ ]" in the reaction.

Table 9. Reactions of cyclohexylidenemalononitrile or isopropylidenemalononitrile with *t*-BuHgI in Me_2SO[a]

$(R^1)(R^2)=C(CN)_2$ + *t*-BuHgI + [ ] $\xrightarrow{h\upsilon}$ $Me_3CC(R^1)(R^2)CH(CN)_2$

139 **140** R^1, R^2= $(CH_2)_5$

141 **142** R^1, R^2= CH_3

Molar equivalents			Time (h)	% Yield[b]	
t-BuHgI:	KI:	PTSA[c]		**140**	**142**
3 :	0 :	0	23	37[d]	-
3 :	3 :	0	23	68	-
3 :	3 :	3	10	100	-
4 :	8 :	0	18	-	68
2 :	2 :	3	26	-	100

[a] 0.05-0.2 M of cycohexylidenemalononitrile or isopropylidenemalononitrile in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

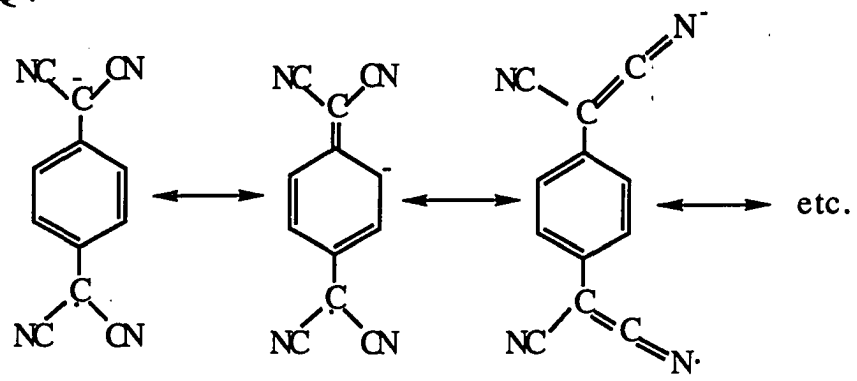
[b] By NMR with toluene as an internal standard.

[c] PTSA is the chemical for "[ ]" in the reaction.

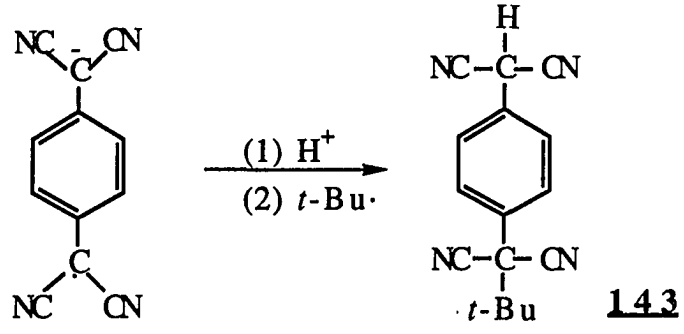
[d] 37% of cyclohexylidenemalononitrile recovered.

Reaction of TCNQ (7,7,8,8-tetracyanoquinodimethane) with *tert*-butyl radical

7,7,8,8-Tetracyanoquinodimethane(TCNQ) is a strong π-acid which forms stable, crystalline anion-radical salts of the type $M^+TCNQ^{\cdot-}$.[11]



Photolysis of TCNQ with *t*-BuHgI/KI in the presence of PTSA gives a high yield of product **143** consistent with the formation and protonation of the anion-radical.

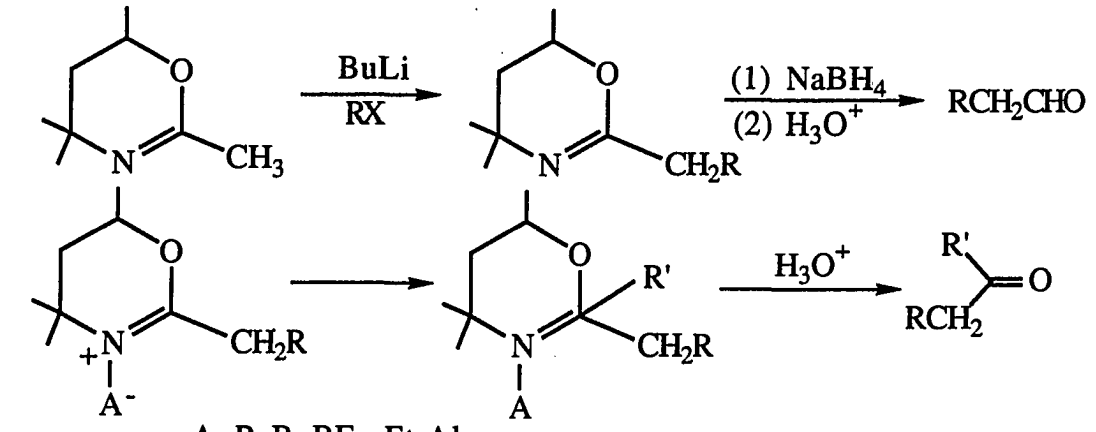


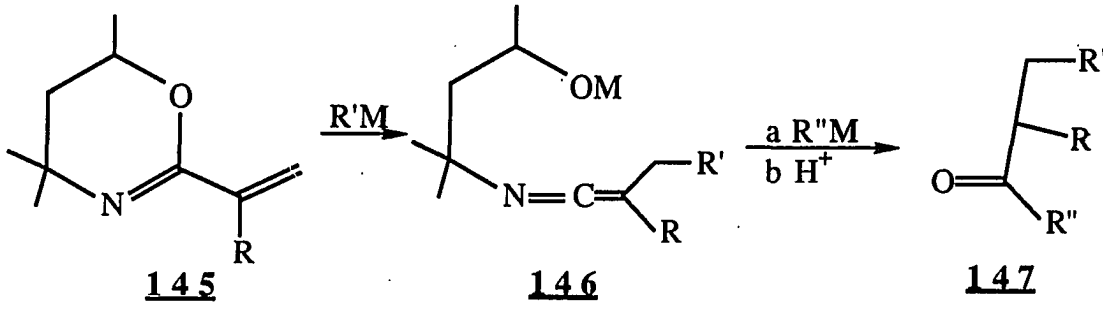
143

In the presence of Dabco the product is a black tar and a trace of α,α'-di-*tert*-butyl-*p*-phenylenedimalononitrile **144** (GCMS only) is formed.

Reactions of *tert*-butyl radicals with 2-(1-alkenyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazines

Meyers[12] reported that the use of dihydro-1,3-oxazine derivatives to synthesize aldehydes, ketones, and carboxylic acids. Similar results for the synthesis of α-substituent aldehydes and kenotes also have been reported.[7]

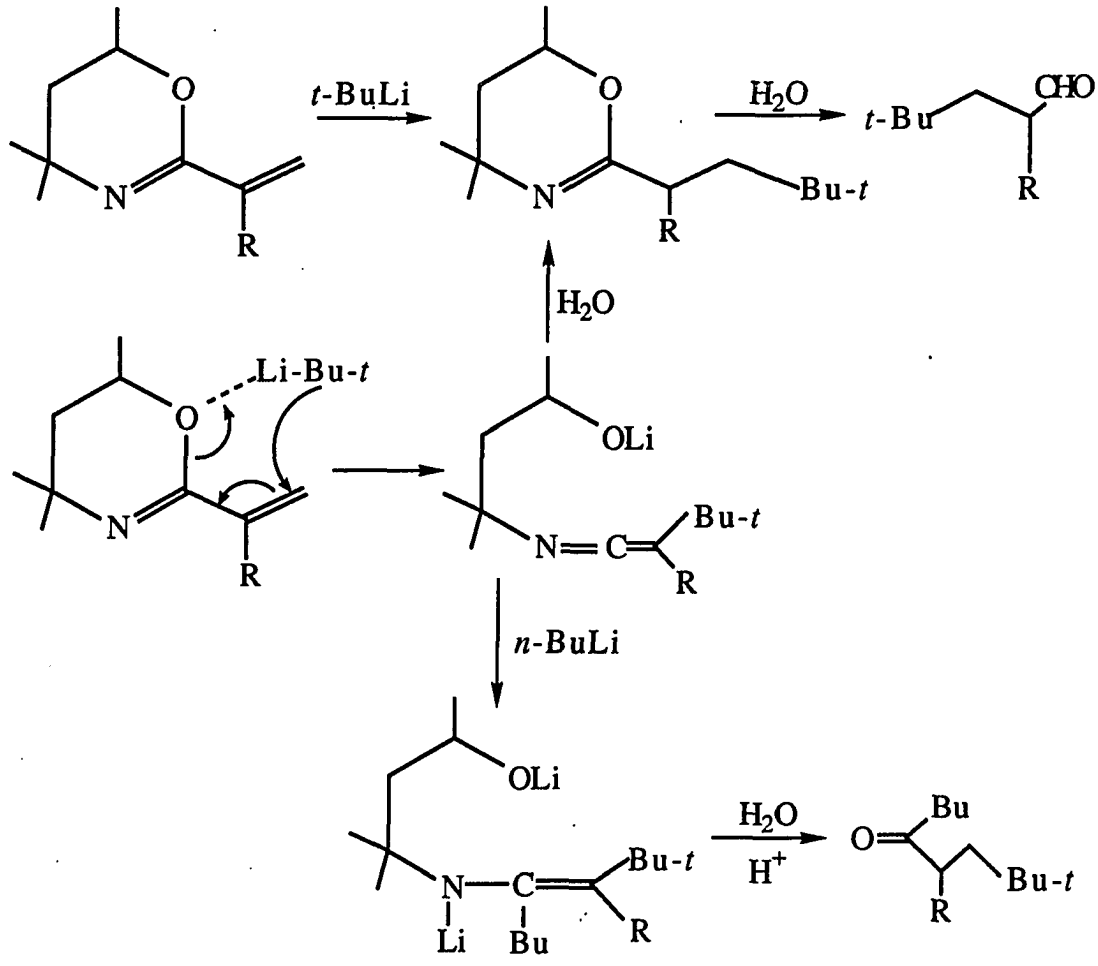




145 **146** **147**

R=Me, Ph

The reaction was proposed to proceed via 1,4-addition to form the ketenimine **146** intermediate which can be hydrolyzed to the aldehyde. Introduction of a base followed by hydrolysis yields the ketone.



Addtion of the *tert*-butyl radicals to the 2-alkenyldihydro-1,3-oxazines gives high yields of the alkylated oxazines in the presence of PTSA and iodide ion. The mechanism is proposed to follow Scheme IV. In the absence of PTSA the major products observed are the dimers of the adduct radicals (Tables 10-12).

Scheme IV

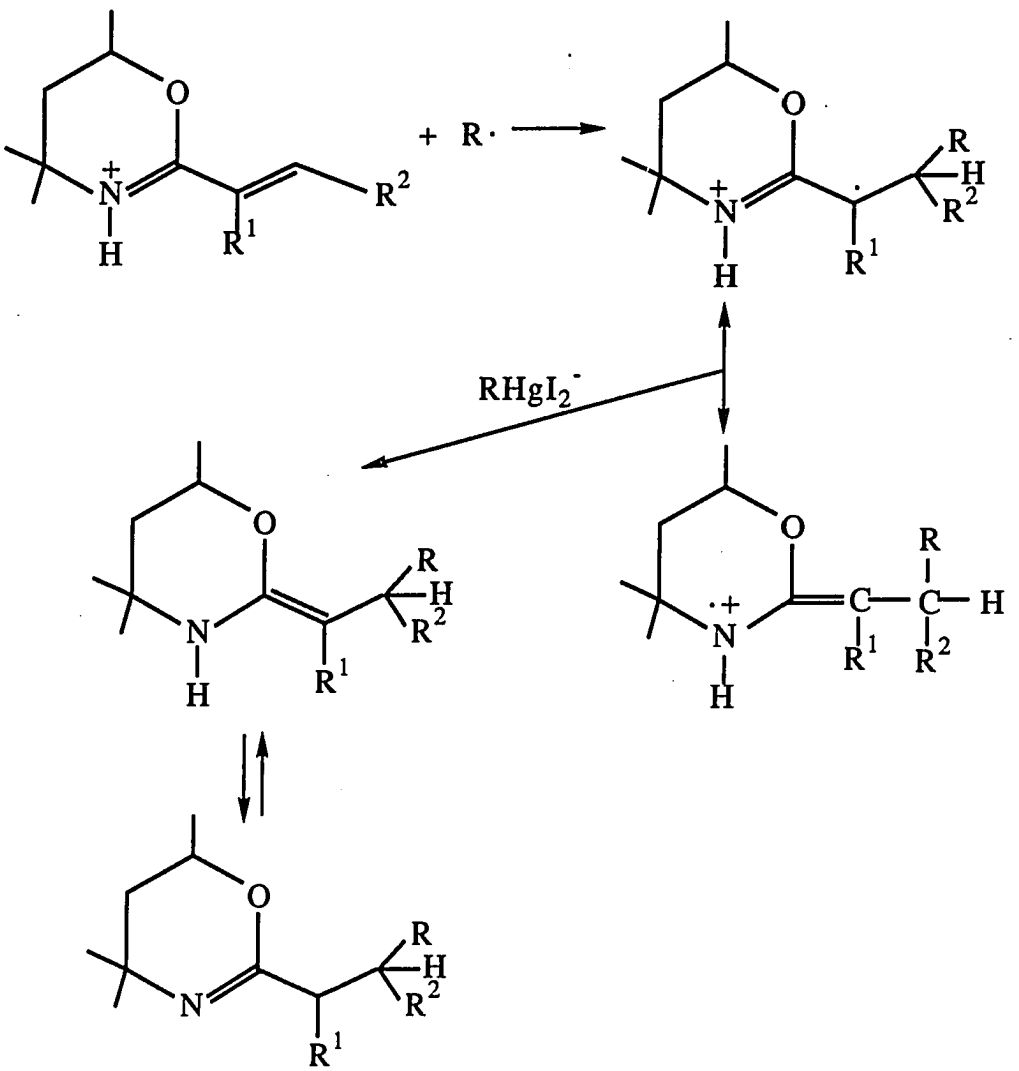
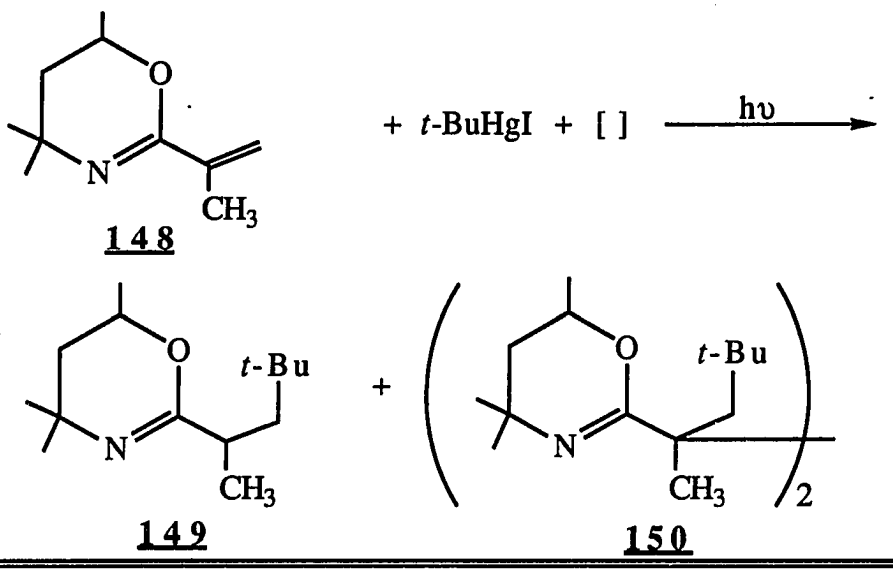


Table 10. Photostimulated reactions of *t*-BuHgI with 2-isopropenyl-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine in Me_2SO[a]



148 **149** **150**

Compound	Molar equivalents *t*-BuHgI:	KI:	D or P[c]	Time (h)	% Yield[b] **149**	**150**
148	2 :	4 :	0	48	~57	~18
148	2 :	4 :	2 (D)	48	~33	~33
148	2 :	4 :	0	38	66[d]	trace
148	5 :	5 :	3 (P)	23	95	

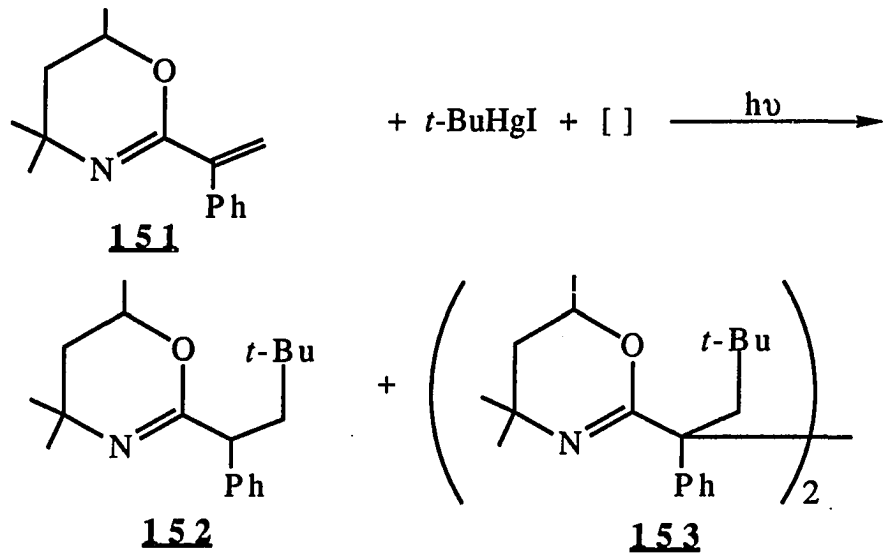
[a] 0.05-0.2 M of oxazines in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

[c] (D) means Dabco; (P) means PTSA, which are the chemical for "[ ]" in the reaction.

[d] HOAc 5 mL with Me_2SO 5 mL.

Table 11. Photostimulated reactions of *t*-BuHgI with 2-(α-syryl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine in Me_2SO[a]



Compound	Molar equivalents *t*-BuHgI:	KI:	D or P[c]	Time (h)	% Yield[b] 152	153
151	5 :	5 : 0		20	trace	~40
151	5 :	5 : 5 (D)		20	trace	~40
151	5 :	5 : 5 (D)		24	trace	>82
151	5 :	5 : 0		20	~13	~24[d]
151	5 :	5 : 5 (P)		20	>95	trace

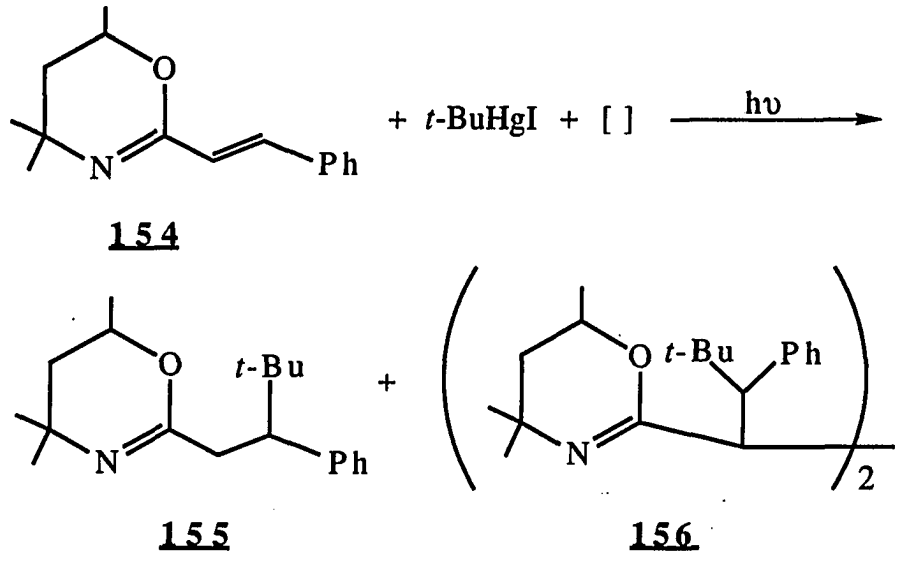
[a] 0.05-0.2 M of oxazines in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

[c] (D) means Dabco; (P) means PTSA, which are the chemical for "[ ]" in the reaction.

[d] HOAc 2 mL with Me_2SO 8 mL.

Table 12. Photostimulated reactions of *t*-BuHgI with 2-(β-styryl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine in Me_2SO[a]



Compound	Molar equivalents *t*-BuHgI:	KI:	PTSA[c]	Time (h)	% Yield[b] **155**	**156**
154	5 :	5 :	0	20	no	reaction
154	5 :	5 :	0	20	63[d]	~30
154	5 :	5 :	5	20	65	~15

[a] 0.05-0.2 M of oxazines in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

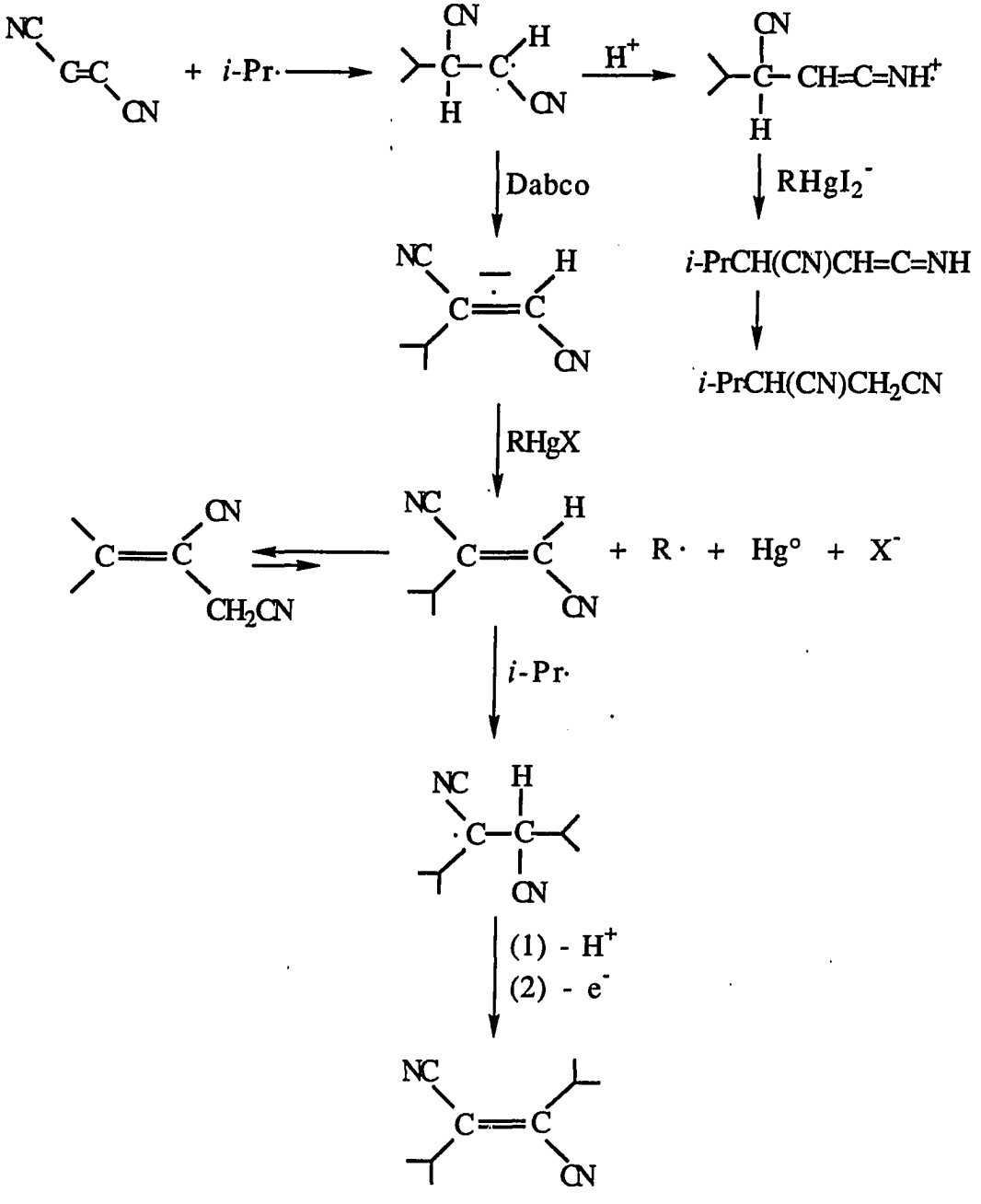
[c] PTSA is the chemical for "[ ]" in the reaction.

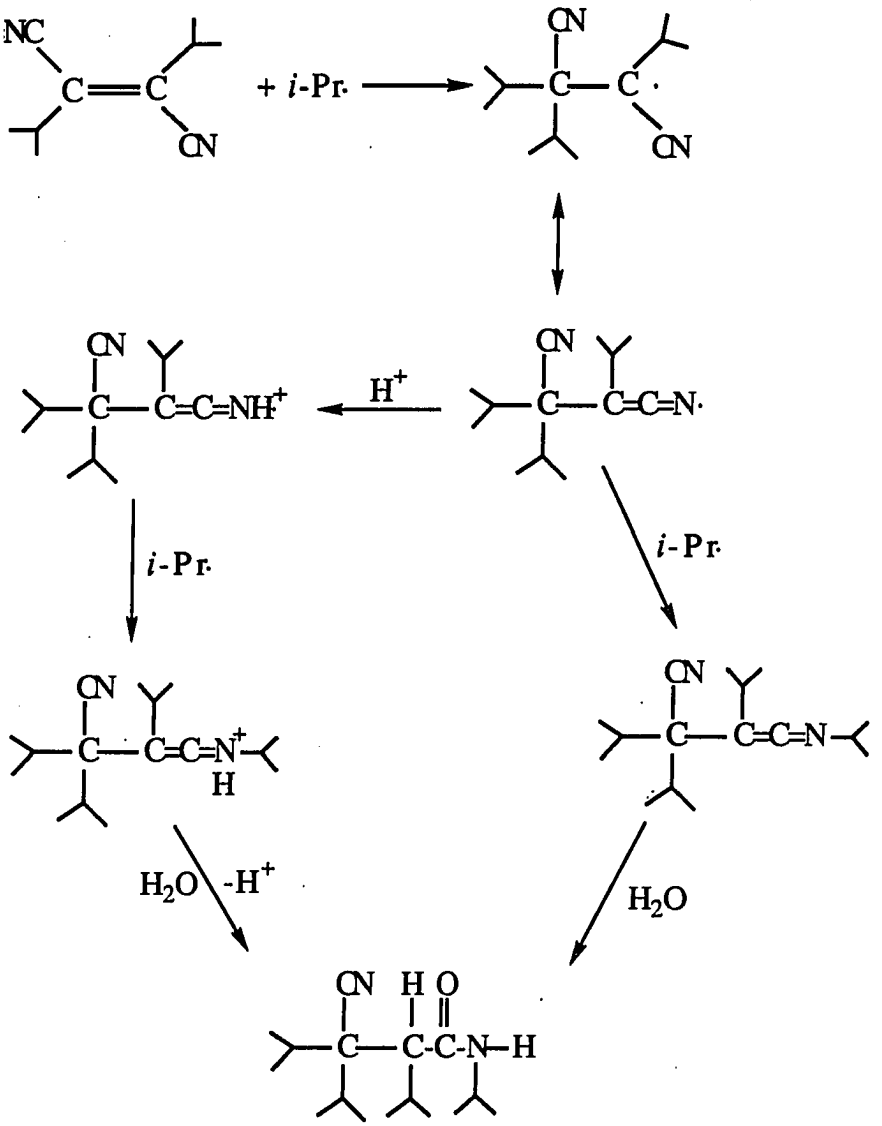
[d] HOAc 2 mL with Me_2SO 8 mL.

Reaction of alkyl radicals with fumaronitrile in the presence of Dabco or PTSA

Fumaronitrile is very reactive toward alkyl radical when compared to other α,β-unsaturated nitriles. By changing the ratio of fumaronitrile, RHgX and Dabco or PTSA, many different products can be synthesized. The mechanism is proposed to follow Scheme V and the results summarized in Tables 13-14.

Scheme V


NC
C=C
CN
+ i-Pr·
CN
H
C
C·
H
CN
H+
CN
C
CH=C=NH+
H
Dabco
RHgI2-
NC
H
C
C
CN
i-PrCH(CN)CH=C=NH
i-PrCH(CN)CH2CN
RHgX
CN
C
C
CH2CN
NC
H
C
C
CN
+ R· + Hg° + X-
i-Pr·
NC
H
C
C
CN
(1) - H+
(2) - e-
NC
C
C
CN


NC
C
C
CN
+ i-Pr·
CN
C
C·
CN
CN
C
C=C=N·
H+
CN
C
C=C=NH+
i-Pr·
i-Pr·
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H2O
CN H O
C
C-C-N-H

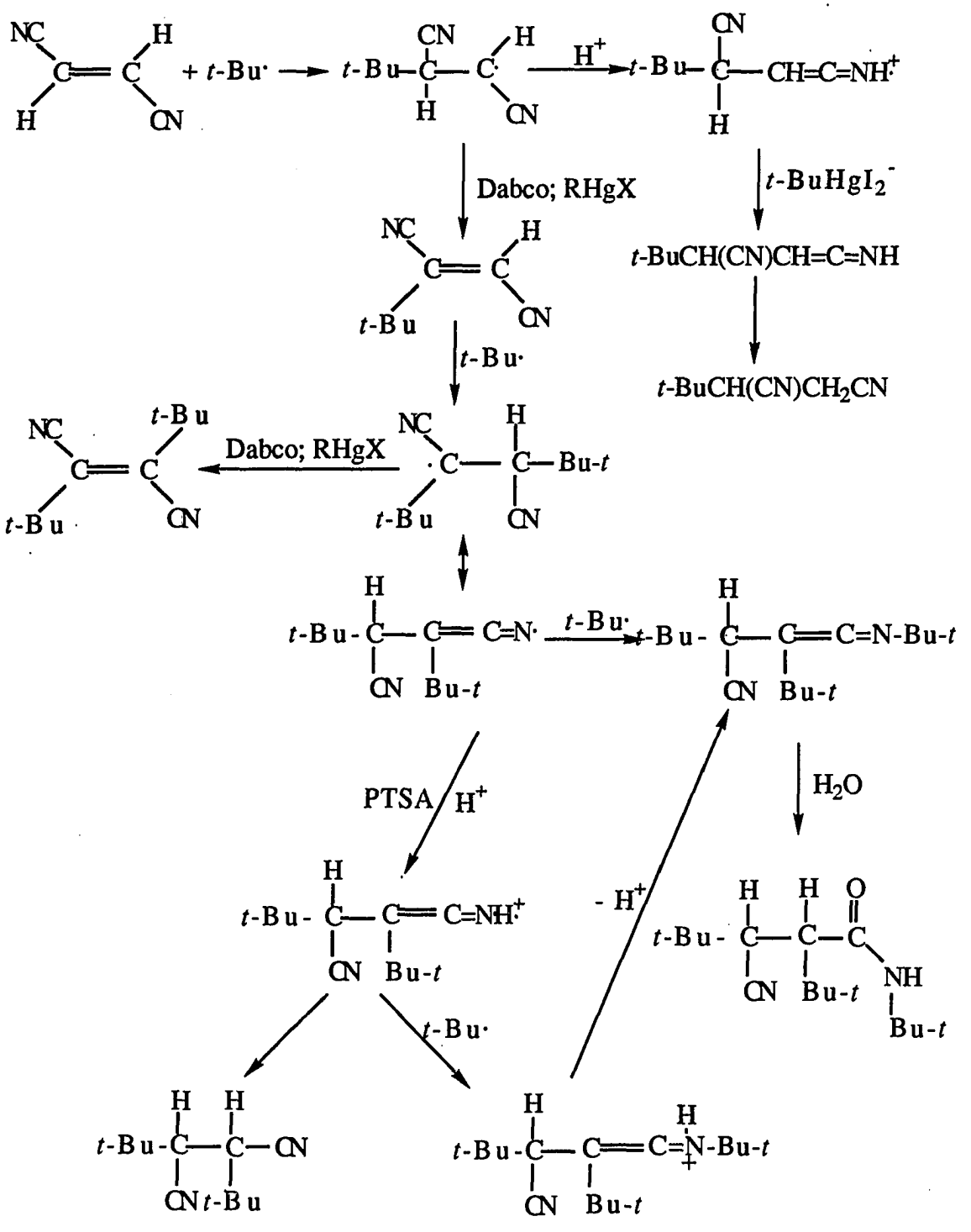
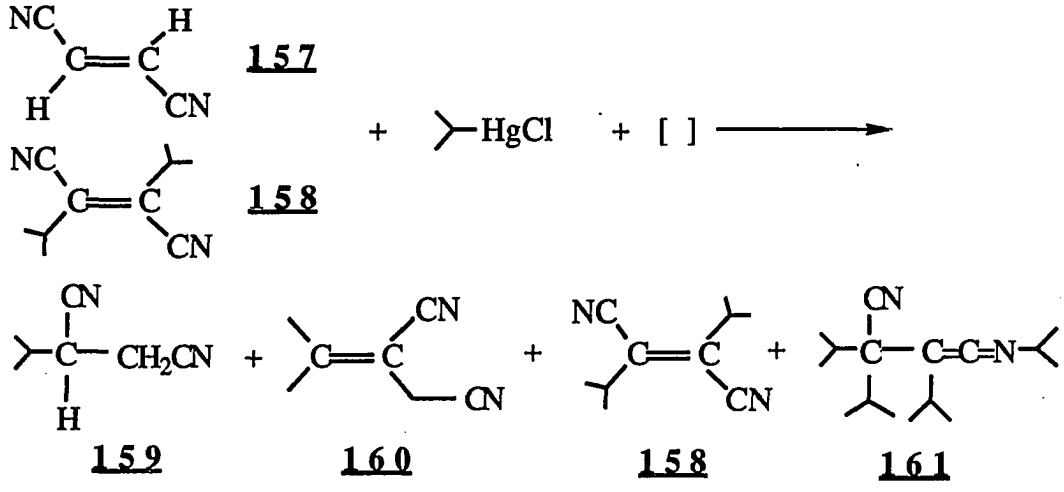

Dabco; RHgX
t-BuHgI2-
t-BuCH(CN)CH=C=NH
t-BuCH(CN)CH2CN
Dabco; RHgX
t-Bu·
PTSA / H+
H2O
- H+

Table 13. Photostimulated reactions of *i*-PrHgCl with fumaronitrile and its derivatives in Me_2SO[a]



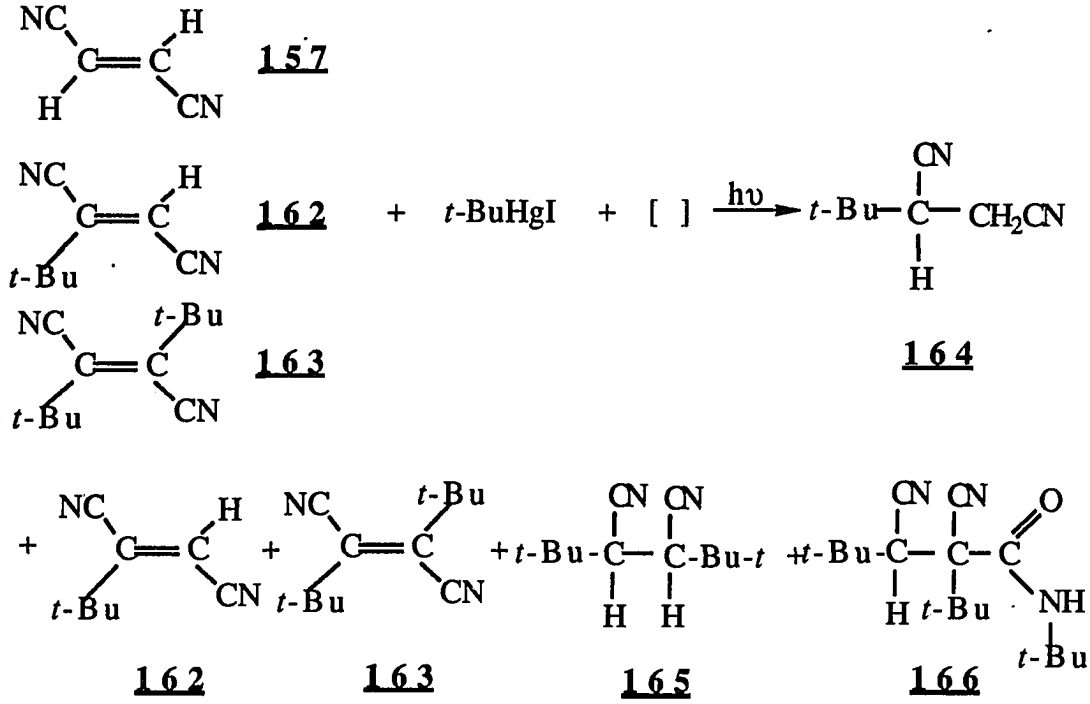
Compound	Molar equivalents *i*-PrHgCl: KI: D or P[c]	Time (h)	% Yield[b] 159	160	158	161
157	2 : 4 : 3 (P)	22	87	-	-	-
157	1 : 2 : 1 (D)	2	-	55	16	-
157	2 : 4 : 2 (D)	2	-	40	48	tr
157	4 : 0 : 4 (D)	20	-	-	-	-
158	5 : 10: 5 (D)	4	-	-	67	33
158	5 : 10: 3 (P)	17	-	-	44	48
158	10 : 20: 3 (P)	48	-	-	tr	83

[a] 0.02-0.2 M of 157 or 158 in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

[c] (D) means Dabco; (P) means PTSA, which are the chemical for "[ ]" in the reaction.

Table 14. Photostimulated reactions of *t*-BuHgI with fumaronitrile and its derivatives in Me_2SO[a]



Comp.	Molar equivalents *t*-BuHgCl: KI: D or P[c]	Time (h)	% Yield[b] 164	162	163	165	166
157	2 : 2 : 2 (P)	23	>95	-	-	-	-
157	2 : 0 : 0	23	tr	-	-	-	-
157	2 : 2 : 0	23	44	14	tr	tr	tr
157	2 : 0 : 4 (D)	2	tr	tr	64	tr	tr
157	1 : 1 : 1 (D)	2	12	82	tr	tr	tr
157	2 : 2 : 2 (D)	3	15	49	31	tr	tr

Table 14. (continued)

Comp.	Molar equivalents *t*-BuHgCl: KI: D or P[c]	Time (h)	% Yield[b] 164	162	163	165	166
157	2 : 2 : 2 (D)	15	15	tr	56	10	-
157	4 : 4 : 4 (D)	2	tr	tr	45	tr	22
157	4 : 4 : 4 (D)	6	tr	20	60	12	tr
162	5 : 5 : 5 (D)	2	-	-	60	-	9
162	5 : 5 : 3 (P)	24	-	-	-	75	8[d]
163	5 : 5 : 3 (P)	24	-	-	71	-	14

[a] 0.01-0.2 M of **157** **162** or **163** in 10 mL of Me_2SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

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

[c] (D) means Dabco; (P) means PTSA, which are the chemical for "[ ]" in the reaction.

[d] A small amount of $Me_3CH(CN)COCMe_3$ (**167**) also was isolated presumably from hydrolysis of **163**.

CONCLUSION

The photostimulated reductive alkylation of α,β-unsaturated nitriles or of 2-(1-alkenyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazines by *t*-BuHgI/KI occurs in high yields in the presence of proton donors such as *p*-$CH_3C_6H_4SO_3H$. Protonation of the intermediate adduct radicals promotes the electron transfer between the adduct radical and the ate-complex, *t*-$BuHgI_2^-$.

EXPERIMENTAL SECTION

General considerations

^{1}H NMR spectra were recorded on a Nicolet Magnetic Corp. NMC-1280 spectrometer (300 MHz) in $CDCl_3$. Product yields were determined by 1H NMR integration with a known amount of toluene as an internal standard. Gas chromatographic analysis was performed on a 3700 varian gas chromatograph with a packed chromosorb W (80-100 mesh) column coated with 7% OV-3 and a thermal conductivity detector. Product yields were determined by addition of a known amount of toluene as an internal standard. The silica gel for column chromatography was purchased from Aldrich Chemical Co. (grade 60, 230-400 mesh, 60Å) and medium-pressure flash column chromatography was routine used.

tert-Butylmercury chloride and iodide were prepared as previously described (see Part II). Dabco, acrylonitrile, crotononitrile, α-chloroacrylonitrile, α-phenylcinnamonitrile, methacrylonitrile, benzylidenemalononitrile, TCNQ (7,7,8,8-tetracyanoquinodimethane), 2-isopropenyl-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine and fumaronitrile were purchased from Aldrich Chemical Company and used without further purification. Cyclohexylidene and isopropylidene malononitrile were prepared according to literature procedures.[13] 2-(α-Styryl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine was prepared by modifing the literature procedures.[7]

2-(β-Styryl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine was

prepared by modifing the literature procedure.[7] To a 100-mL round bottle flask equipped with a thermometer, a stirrer, and a 50-mL addition funnel was added 20 mL of concentrated (95-97%) sulfuric acid. The acid was cooled to 0-5 °C with an ice bath and 10 mL of cinnamonitrile (80 mmol) was added at such a rate that the temperature was maintained at 0-5 °C. After the addition of the nitrile was complete, 15 mL (118 mmol) of 2-methyl-2,4-pentanediol was added at a rate that the same temperature was maintained at 0-5 °C. The mixture was stirred for an additional 2 days and then poured into about 200 of crushed ice. The aqueous solution was extracted with four 25-mL portions of dichloromethane. The aqueous solution was made alkaline with 40% sodium hydroxide solution; ice was periodically added during the addition of the sodium hydroxide solution to keep the mixture cool (below 35 °C). Upon becoming basic, a yellow oil appeared, which was separated. The aqueous layer was extracted with four 25-mL portions of dichloromethane and dried over anhydrous potassium carbonate. The solvent was removed by rotary evaporation, and the residue was purified by flash column chromatography with hexane (95%) - ethyl acetate (5%) to give 2-(β-styryl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine (about 30%); ^{1}H NMR ($CDCl_3$) δ 7.455-7.258(m, 5H), 7.254(d, *J*=15.9 Hz, 1H), 6.448(d, *J*=16.2 Hz, 1H), 4.215(m, 1H), 1.749(dd, *J*=13.5, 2.1 Hz, 1H), 1.389(d, *J*=13.2 Hz, 1H), 1.346(d, *J*=6.3 Hz, 3H), 1.253(3H), 1.217(3H); GC and HRMS, m/z (relative intensity) 229.144667(M^+, 15, calcd for $C_{15}H_{19}NO$ 229.14666), 214(13), 131(100), 103(32), 77(17).

General procedure for the photostimulated alkylation of acrylonitrile

Acrylonitrile (0.5 mmol), *t*-BuHgI (2.5 mmol), KI (2.5 mmol) and PTSA (2.5 mmol) were placed in a pyrex test tube and 10 mL of deoxygenated Me_2SO was added under nirogen. With stirring the solution was irradiated with a 275-W sunlamp ca. 25 cm from the reaction test tube for 23 hours. The reaction mixture was then poured into 25 mL of saturated sodium thiosulfate solution, neutralized with $NaHCO_3$ solution and then extracted three times with 25 mL portions of methylene chloride. The combined organic extract was washed three times with the saturated sodium thiosulfate and once with brine solution, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The mixture was analyzed by ^1H NMR and each compound was isolated by flash column chromatography with hexane (98%)-ethyl acetate (2%) to give 40% of **116** and 35% of **117** (by ^1H NMR).

4,4-Dimethylpentanenitrile (**116**)[14]

The compound was an oily liquid: ^1H NMR ($CDCl_3$) δ 2.44-2.26(m, 2H), 1.69-1.59(m, 2H), 0.923(s, 9H); GCMS m/z (relative intensity) 112($M+H^+$, 3), 96(85), 69(31), 57(100), 41(66).

4,4-Dimethylpentanamide (**117**)[15]

The compound was a white powder, mp 118-121 °C (lit.[15] mp 140-141 °C); FTIR ($CDCl_3$) at 3352, 3188, 1666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.21(br, 1H), 5.77(br, 1H), 2.22-2.16(m, 2H), 1.58-1.52(m, 2H), 0.904(s, 9H); ^{13}C NMR ($CDCl_3$) δ 176.7, 39.2, 31.5, 30.0, 29.0; GC and

HRMS, m/z (relative intensity) 129.11498(M^+, 1.5, calcd for $C_7H_{15}NO$ 129.11536), 114(31), 97(17), 73(65), 72(100), 57(39).

General procedure for photostimulated alkylations of acrylonitrile in Me_2SO-EtOH

Acrylonitrile (1.0 mmol), *t*-BuHgI (2.5 mmol), KI (2.5 mmol) and PTSA (2.5 mmol) were placed in a pyrex test tube and 5 mL of deoxygenated Me_2SO and 5 mL of EtOH were added under nitrogen. With stirring the solution was irradiated with a 275-W sunlamp ca. 25 cm from the reaction test tube for 24 hours. Worked up followed the procedure given above. The products were analyzed by ^1H NMR using toluene as an internal standard to give **116** (13%), **117** (13%), and **118** (>18%). Flash column chromatography was used to separate **118** as a liquid.

Ethyl 4,4-dimethylpentanoate (**118**)[14]

Compound **118** was isolated as a liquid; ^1H NMR ($CDCl_3$) δ 4.18-4.08(m, 2H), 2.30-2.24(m, 2H), 1.57-1.52(m, 2H), 1.257(t, *J*=7.2 Hz, 3H), 0.896(s, 9H); FTIR ($CDCl_3$) at 1734 cm^{-1}; GC and HRMS, m/z (relative intensity) 159.11691($M+H^+$, 0.5, calcd for $C_9H_{19}O_2$ 159.1385), 158.13253(M^+, 0.3, calcd for $C_9H_{18}O_2$ 158.1307), 143.10728($M-15^+$, 21.2, calcd for $C_8H_{15}O_2$ 143.1072), 113.09712($M-45^+$, 33.2, calcd for $C_7H_{1}O$ 113.0967), 102.06845($M-56^+$, 59.1, calcd for $C_5H_{10}O_2$ 102.0681), 97(52), 85(7), 74(26), 69(66), 57(100), 41(55); GCMS (CI, ammonia), m/z (relative intensity) 334($2M+18^+$,

0.2), 193($M+35^+$, 24), 176($M+18^+$, 100), 159($M+1^+$, 2.2).

Photostimulated reaction of crotononitrile (mixture of *E* and *Z* isomers) with *t*-BuHgI in the presence of PTSA

A mixture of crotononitrile (2 mmol), *t*-BuHgI (4 mmol), KI (4 mmol) and PTSA (6 mmol) in 10 mL of Me_2SO was irradiated under nitrogen. After irradiation, the solution was worked up as described previously and analyzed by ^1H NMR using toluene as internal standard to give 60% of 3,4,4-trimethylpentanenitrile (**120**) and 12% of 3,4,4-trimethylpentanamide (**121**).

3,4,4,-Trimethylpentanenitrile (**120**)

Compound **120** was isolated by flash column chromatography with hexane (99.5%)-ethyl acetate (0.5%) as a liquid; The ^1H NMR ($CDCl_3$) δ 2.47(dd, *J*=16.8, 3.6 Hz, 1H), 2.06(dd, *J*=16.8, 10.2 Hz, 1H), 1.74-1.62(m, 1H), 1.07(d, *J*=6.9 Hz, 3H), 0.897(s, 9H); GCMS, m/z (relative intensity) 126($M+1^+$, 0.7), 110(18), 93(2), 85(6), 69(39), 57(100), 41(51).

3,4,4-Trimethylpentanamide (**121**)

Compound **121** was isolated as a colorless solid, mp: 162-163 °C; FTIR at 3344, 3179, 1641 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.91(br, 1H), 5.54(br, 1H), 2.49-2.33(m, 1H), 1.85-1.73(m, 2H), 0.91(d, *J*=6.0 Hz, 3H), 0.88(s, 9H); GC and HRMS, m/z (relative intensity) 143.1309(M^+, 14, calcd for $C_8H_{17}NO$ 143.13101), 128(17), 124(5), 110(6), 87(61),

72(71), 59(100), 57(91).

General procedure for photostimulated alkylations of α-chloroacrylonitrile

A mixture of α-chloroacrylonitrile (1 mmol), *t*-BuHgI (5 mmol), KI (5 mmol) and PTSA (5 mmol) in 10 mL of Me_2SO was irradiated under nitrogen. The work-up procedure was similar to that described previously. The product was analyzed by GC to contain 65% of 2-chloro-4,4-dimethylpentanenitrile (**123**) and 13% of 2,2,7,7-tetramethyl-4-octene-4,5-dinitrile (**124**).

2-Chloro-4,4,-dimethylpentanenitrile (**123**)[8]

Compound **123** was isolated by flash column chromatography with hexane (95%) - ethyl acetate (5%); ^1H NMR ($CDCl_3$) δ 4.44(dd, *J*=9.0, 5.4 Hz, 1H), 2.7(dd, *J*=14.4, 9.0 Hz, 1H), 1.98(dd, *J*=14.4, 5.4 Hz, 1H), 1.046(s, 9H); ^{13}C NMR ($CDCl_3$) δ 118.1, 56.2, 39.3, 31.1, 29.3; GC and HRMS, m/z (relative intensity) 148($M+2^+$, 0.1), 146(M^+, 0.2), 130.04210($M-16^+$, 8, calcd for C_6H_9ClN 130.04235), 94(34), 89(6), 67(24), 57(100). The ^1H NMR was the same as the spectra data in literatue.[8]

2,2,7,7-Tetramethyl-4-octene-4,5-dinitrile(**124**)

Compound **124** was isolated as solid, mp 103-104 °C (hexane); ^1H NMR ($CDCl_3$) δ 2.533(s, 4H), 1.088(s, 18H); ^{13}C NMR ($CDCl_3$) δ 129.0, 117.0, 47.5, 33.9, 29.4; GC and HRMS, m/z (relative intensity)

218.17818(M^+, 0.4, calcd for $C_{14}H_{22}N_2$ 218.17830), 162(1), 147(7), 105(3), 57(100); GCMS (CI, isobutane), m/z (relative intensity) 437(2M+1$^+$, 3), 275(M+57$^+$, 100), 219(M+1$^+$, 31).

Photostimulated alkylations of ethyl (*E*)-α-cyanocinnamate

A mixture of ethyl (*E*)-α-cyanocinnamate (0.5 mmol), *t*-BuHgI (2 mmol), KI (2 mmol) and PTSA (2 mmol) in 10 mL of Me_2SO was irradiated under nitrogen. After workup by the procedure described previously the product was analyzed by ^1H NMR to give 83% of ethyl β-*tert*-butyl-α-cyano-β-phenylpropionate (**126**).

Ethyl β-*tert*-butyl-α-cyano-β-phenylpropionate (**126**)

The compound **126** was isolated as a mixture of two diastereomers which showed one peak by GC and were not separable by flash column chromatography; ^1H NMR indicated a mixture of two isomers (about 3:1); ^1H NMR ($CDCl_3$) δ 7.42-7.16(m), 4.05-3.90(m), 3.85(d, *J*=9.0 Hz), 3.29(d, *J*=9.0 Hz), 3.14(d, *J*=5.1 Hz), 1.09(s), 1.06(s), 0.98(t, *J*=7.2 Hz); GC and HRMS, m/z (relative intensity) 259.15729(M^+, 9, calcd for $C_{16}H_{21}NO_2$ 259.15723), 244(2), 203(8), 186(7), 176(24), 130(25), 91(21), 77(5), 57(100).

General procedure for photostimulated alkylations of methacrylonitrile

Methacrylonitrile (2 mmol), *t*-BuHgI (10 mmol), KI (10 mmol) and Dabco (5 mmol) were placed in 10 mL of Me_2SO and irradiated

under nitrogen. After workedup the products were analyzed as a mixture of 60% of 2,4,4-trimethylpentanenitrile (**128**) and 25% of 2,3-dimethyl-2,3-bis(2,2-dimethylpropyl)butanedinitrile (**129**).

2,4,4-Trimethylpentanenitrile (**128**)

Compound **128** was isolated by flash column chromatography with hexane (99.5%)- ethyl acetate (0.5); FTIR at 2235 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65-2.53(m, 1H), 1.73(dd, *J*=14.1, 10.2 Hz, 1H), 1.34(d, *J*=7.2 Hz, 3H), 1.32(dd, *J*=14.1, 3.0 Hz, 1H), 0.997(s, 9H); GC and HRMS, m/z (relative intensity) 126($M+1^+$, 5), 110(42), 83(10), 69(32), 57(100), 41(50).

2,3-Dimethyl-2,3-bis(2,2-dimethylpropyl)butanedinitrile (**129**)

Compound **129** was formed as 1:1 mixture of diasteromers on judged from ^1H NMR analysis of the crude product. The diasteromers were separated by column chromatography. One diasteromer had mp 122-123 °C and ^1H NMR ($CDCl_3$) δ 1.86(d, *J*=14.1 Hz, 2H), 1.59(s, 6H), 1.50(d, *J*=14.1 Hz, 2H), 1.15(s, 18H); GC and HRMS, m/z (relative intensity) 248.22553 (M^+, calcd for $C_{16}H_{28}N_2$ 248.22525), 191(0.8), 177(45), 125(18), 110(10), 94(3), 68(27), 57(100). The other diastereomer was not isolated in pure form. A mixture of the two diastereomers having mp 78-85 °C was separated and from this mixture the ^1H NMR and MS of the second diastereomer could be measured; ^1H NMR ($CDCl_3$) δ 1,84(d, *J*=14.1 Hz, 2H), 1.58(s, 6H), 1.53(d, *J*=14.1 Hz, 2H), 1.16(s, 18H); GCMS, m/z (relative intensity) 249($M+1^+$,

0.7), 233(6), 191(0.8), 177(42), 125(18), 110(12), 94(3), 68(26), 57(100).

Photostimulated reaction of α-phenylcinnamonitrile with *t*-BuHgI in the presence of Dabco

A mixture of α-phenylcinnamonitrile (1 mmol), *t*-BuHgI (5 mmol), KI (5 mmol) and PTSA (5 mmol) in 10 mL of Me_2SO was irradiated for 36 h under nitrogen. After irradiation, the solution was worked up and analyzed by ^1H NMR to give about 50% of **131**, about 20% of **132** and about 20% of **133**. Each compound was present as a mixture of two diastereomers.

4,4-Dimethyl-2,3-diphenylpentanenitrile (131)

There were two diastereomers for compound **131**. One of the diastereomers having mp 101-102 °C was isolated by flash column chromatography. This diastereomer had ^1H NMR ($CDCl_3$) δ 7.25-6.94(m, 10H), 4.41(d, *J*=3.6 Hz, 1H), 3.66(d, *J*=3.6 Hz, 1H), 1.138(s, 9H); GC and HRMS, m/z (relative intensity) 263.16718(M^+, 0.8, calcd for $C_{19}H_{21}N$ 263.16740), 248(0.3), 206(1), 180(38), 147(86), 116(15), 105(73), 91(100), 77(10), 57(48). The other pure diastereomer had ^1H NMR ($CDCl_3$) δ 4.08(d, *J*=10.2 Hz, 1H), 3.08(d, *J*=10.2 Hz, 1H), 1.145(s, 9H); GCMS, m/z (relative intensity) 263(0.6), 248(0.5), 180(91), 147(81), 116(22), 105(70), 91(100), 77(13), 57(74).

2-(4-*t*-Butylphenyl)-3-phenyl-4,4-dimethylpentanenitrile (**132**)

A mixture of two diastereomers were isolated by column chromatography. The mixture gave a single peak in GC and just one spot in TLC. The mixture had ^{1}H NMR ($CDCl_3$) δ 7.22-6.88(m), 4.37(d, *J*=3.6 Hz), 4.07(d, *J*=9.6 Hz), 4.05(d, *J*=9.6 Hz), 2.66(d, *J*=3.6 Hz), 1.24(s), 1.197(s), 1.132(s), 1.117(s). The mixture of diastereomers were separated by the capillary column used in GCMS. One of the isomers had GCMS, m/z (relative intensity), 319(M^+, 1.8), 262(0.1), 248(0.5), 236(3), 225(4), 221(4), 173(20), 147(85), 105(70), 91(100), 77(7), 57(31). The other had 319(M^+, 1.4), 262(0.1), 248(0.8), 236(7), 221(7), 173(21), 147(90), 105(74), 91(100), 77(5), 57(30).

N-*t*-Butyl-4,4-dimethyl-2,3-diphenylpentanamide (**133**)

Column chromatography with hexane (95%) -ethyl acetate (5%) give two diastereomers which were recrystallized from hexane - methylene chloride. One of the diastereomers had mp 207-208 °C; FTIR ($CDCl_3$) at 3346, 1643 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.57-7.15(m, 10H), 4.96(br, 1H), 3.72(d, *J*=11.7 Hz, 1H), 3.31(d, *J*=11.7 Hz, 1H), 0.839(s, 9H), 0.649(s, 9H); ^{13}C NMR ($CDCl_3$) δ 171.7, 142.9, 140.0, 128.9, 128.2, 127.5, 127.0, 126.0, 58.5(d), 58.0(d), 50.6, 34.6, 29.8(q), 28.1(q); GC and HRMS, m/z (relative intensity) 337.23972(M^+, 1.3, calcd for $C_{23}H_{31}NO$ 337.24056), 322(0.2), 281(3), 238(2), 182(13), 167(15), 105(4), 91(11), 77(2), 57(100). The other pure diastererisomer had mp 143-146 °C, FTIR ($CDCl_3$) at 3337, 1661 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.07-6.84(m, 10H), 5.34(br, 1H), 3.75(d, *J*=10.2 Hz,

1H), 3.64(d, J=10.2 Hz, 1H), 1.232(s, 9H), 0.974(s, 9H); GCMS, m/z (relative intensity) 337(M^+, 2.1), 322(0.5), 281(9), 238(0.3), 182(23), 167(9), 105(9), 91(27), 77(3), 57(100).

General procedure for photostimulated alkylations of benzylidenemalononitrile, cyclohexylidenemalononitrile, isopropylidenemalononitrile and TCNQ (7,7,8,8-tetracyanoquinodimethane)

The substrate (0.5-2.0 mmol), RHgX and coreactants were dissolved in 10 mL of deoxygenated Me_2SO in a pyrex test tube equipped with a rubber septum. The mixture was irradiated under nitrogen by a 275-W General electric sunlamp ca. 25 cm from the reaction tube. The reaction was quenched with aqueous sodium thiosulfate and extracted with methylene chloride. The methylene chloride extract was washed three times with aqueous sodium thiosulfate and one time with brine solution, dried over Na_2SO_4, and the solvent evaporated. The ^1H NMR yield was determined with an internal standard (toluene). If necessary, the products were isolated by flash column chromatography (silica gel) with hexane (95-99%) - ethyl acetate (1-5%).

(2,2-Dimethyl-1-phenylpropyl)malononitrile (**135**)[19]

The compound had ^1H NMR ($CDCl_3$) δ 7.38(br, s, 5H), 4.22(d, J=5.7 Hz, 1H), 3.00(d, J=5.7 Hz, 1H), 1.08(s, 9H); ^{13}C NMR ($CDCl_3$) δ 136.2, 129.0, 128.4, 128.1, 113.3, 113.2, 56.3, 34.7, 28.2, 24.9; GC and HRMS, m/z (relative intensity) 212.13154(M^+, 7, calcd for $C_{14}H_{16}N_2$

212.13135), 197(3), 156(1), 132(6), 105(2), 91(7), 77(4), 57(100).

α-Cyano-β-*tert*-butylcinnamonitrile (**136**)[16]

This compound was isolated as a solid, mp 108-112 °C (lit.[16] mp 114.5-115 °C) and had ^{1}H NMR ($CDCl_3$) δ 7.47-7.40(m, 3H), 7.08-7.05(m, 2H), 1.362(s, 9H); HRMS, m/z (relative intensity) 210.11602(M^+, 78, calcd for $C_{14}H_{14}N_2$ 210.11570), 195(100), 168(98), 153(21), 141(17), 128(10), 115(19), 104(14), 91, 77, 57.

1,2-Diphenylethylmalononitrile (**137**)[17]

This compound had ^{1}H NMR ($CDCl_3$) δ 7.42-7.16(m, 10H), 3.83(d, *J*=5.1 Hz, 1H), 3.45(dd, *J*=7.5, 5.4 Hz, 1H), 3.24(d, *J*=6.9 Hz, 2H); GC and HRMS, m/z (relative intensity) 246.11576(M^+, 10.4, calcd for $C_{17}H_{14}N_2$ 246.11570), 181(4), 165(2), 129(4), 103(3), 91(100), 77(5).

Benzylmalononitrile (**138**)[17,18]

The compound was isolated as a white solid, mp 81-83 °C (lit.[17,18] mp 88-87 °C, 91-92 °C); ^{1}H NMR ($CDCl_3$) δ 7.39-7.30(m, 5H), 3.90(td, *J*=7.2, 0.6 Hz, 1H), 3.27(d, *J*=6.9 Hz, 2H); GC and HRMS, m/z (relative intensity) 156.0690(M^+, 17, calcd for $C_{10}H_8N_2$ 156.06875), 129(2), 103(1), 91(100), 77(4), 65(14).

1-(1,1-Dimethylethyl)cyclohexylmalononitrile (**140**)

The compound was isolated as solid, mp 49-53 °C; ^{1}H NMR ($CDCl_3$) δ 4.29(s, 1H), 1.92-1.22(m, 10 H), 1.14(s, 9H); GC and HRMS,

m/z (relative intensity) 203.15507(M-1$^+$, very small, calcd for $C_{13}H_{19}N_2$ 203.15482), 189.13953(M-15$^+$, 6, calcd for $C_{12}H_{17}N_2$ 189.13817), 148(0.4), 133(0.4), 121(3), 81(2), 67(2), 57(100).

1,1,2,2-Tetramethylpropylmalononitrile (**142**)

Compound **142** was isolated as a solid, mp 100-101 °C; ^{1}H NMR ($CDCl_3$) δ 3.727(s, 1H), 1.246(s, 6H), 1.049(s, 9H); GC and HRMS, m/z (relative intensity) 163.12356(M-1$^+$, very small, calcd for $C_{10}H_{15}N_2$ 163.12352), 149.10780(M-15$^+$, 10, calcd for $C_9H_{13}N_2$ 149.10787), 122(1), 108(9), 99(2), 93(0.4), 83(23), 69(7), 57(100).

α-*tert*-Butyl-*p*-phenylenedimalononitrile (**143**)

Compound **143** was isolated by flash column chromatography with hexane (93%) - ethyl acetate (7%) to remove impurities and then removed from the column with pure ethyl acetate. The mp was 113-117 °C; ^{1}H NMR ($CDCl_3$) δ 7.68(qt, *J*=8.4, 2.1 Hz, 4H), 5.21(br, 1H), 1.221(s, 9H); ^{13}C NMR ($CDCl_3$) δ 131.7, 129.4, 128.2, 127.6, 114.3, 111.2, 52.4, 41.8, 27.9, 25.5; GC and GCMS, m/z (relative intensity) 262(M$^+$, 0.4), 247.09874(M-15$^+$, 3.4, calcd for $C_{15}H_{11}N_4$ 247.09837), 220(0.7), 182(2), 141(1), 114(1), 77(0.5), 57(100); GCMS (CI, isobutane), m/z (relative intensity) 525(2M+1, 4), 319(M+57$^+$, 100), 263(M+1$^+$, 46), 249(84), 207(8); GCMS (CI, methane), m/z (relative intensity) 525(2M+1$^+$, very small), 303(M+41$^+$, 2), 291(M+29$^+$, 13), 263(M+1$^+$, 41), 247(6), 235(21), 221(3), 207(100).

Compound **144** was observed in GCMS only, m/z (relative

intensity) 303(M-15$^+$, 0.2), 247(0.1), 77(0.2), 57(100).

General procedure for photostimulated alkylations of oxazines

The substrate (0.5-2 mmol), *t*-BuHgI and coreactants were dissolved in 10 mL of deoxygenated Me_2SO in a pyrex test tube equipped with a rubber septum. The mixture was irradiated under nitrogen by a 275-W General Electric sunlamp ca. 25 cm from the reaction tube. The reaction was quenched with aqueous sodium thiosulfate, neutralized, and then extracted with methylene chloride. The methylene chloride extract was washed three times with aqueous sodium thiosulfate and one time with brine solution, dried over Na_2SO_4, and the solvent evaporated. The yields of the products were determined by ^1H NMR by using toluene as an internal standard and if necessary, the products were isolated by column chromatography (silica gel) with hexane (95%) - ethyl acetate (5%).

2-(1,3,3-Trimethylbutyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine (**149**)[7]

Compound **149** was a colorless liquid which had ^1H NMR ($CDCl_3$) δ 4.06(m, 1H), 2.38(m, 1H), 1.83-1.61(m, 2H), 1.31-1.02(m, 14H), 0.89, 0.88(9H); GC and HRMS, m/z (relative intensity) 225(M$^+$, 1), 224.20135(M-1$^+$, 2, calcd for $C_{14}H_{26}NO$ 224.20144), 210.108605(M-15$^+$, 47, calcd for $C_{13}H_{24}NO$ 210.18579), 183(7), 168(100), 154(12), 141(6), 126(16), 111(11), 83(15), 69(11), 57(53).

2,2,4,5,7,7-Hexamethyl-4,5-bis(4,4,6-trimethyl-5,6-dihydro-1,3-oxazin-2-yl)octane (**150**)

Compound **150** was a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 4.00(m, 2H), 2.32-1.07(m, 34 H), 0.874, 0.866(18H); GC and HRMS, m/z (relative intensity) 447.39587($M\text{-}1^+$, very small, calcd for $C_{28}H_{51}N_2O_2$ 447.39505), 433.37907($M\text{-}15^+$, 1.3, calcd for $C_{27}H_{49}N_2O_2$ 433.37940), 391(1.2), 333(0.5), 224(31), 208(4), 182(2), 168(100), 126(12), 57(36); GCMS (CI, ammonia), m/z (relative intensity) 449($M+1^+$, 100).

2-(3,3-Dimethyl-1-phenylbutyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine (**152**)

Compound **152** was a liquid; ^{1}H NMR ($CDCl_3$) δ 7.39-7.15(m, 5H), 4.05(m, 1H), 3.52(td, J=9.9, 3.6 Hz, 1H), 2.30-2.18(m, 1H), 1.70-1.43(m, 2H), 1.28-1.07(m, 10H), 0.931, 0.915(9H); GC and HRMS, m/z (relative intensity) 287.22510(M^+, 1, calcd for $C_{19}H_{29}NO$ 287.22491), 272(13), 230(100), 188(5), 168(2), 154(9), 145(14), 131(26), 118(8), 91(11), 57(45).

2,2,7,7-Tetramethyl-4,5-diphenyl-4,5-bis(4,4,6-trimethyl-5,6-dihydro-1,3-oxazin-2-yl)octane (**153**)

Compound **153** was a liquid with FTIR at 1663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.55-7.12(m, 10H), 3.82(m, 1H), 3.48(m, 1H), 2.60-1.03(m, 26H), 0.903(s, 9H), 0.592(s, 9H); GC and HRMS, m/z (relative intensity) 572.43291(M^+, 4, calcd for $C_{38}H_{56}N_2O_2$ 572.43418), 515(100), 332(4), 250(7), 230(8), 205(5), 180(4), 131(14), 103(47), 83(31),

57(100).

2-(3,3-Dimethyl-2-phenylbutyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine (**155**)

Compound **155** was a liquid; ^{1}H NMR ($CDCl_3$) δ 7.23-7.09(m, 5H), 3.48(m, 1H), 2.88(dd, *J*=12.3, 5.4 Hz, 1H), 2.70(dd, *J*=13.8, 5.4 Hz, 1H), 2.48(dd, *J*=13.8, 12.3 Hz, 1H), 1.454(d, *J*=2.4 Hz, 1H), 1.41(d, *J*=2.4 Hz, 1H), 1.08(d, *J*=3.0 Hz, 3H), 1.00(s, 3H), 0.901(s, 9H), 0.70(s, 3H); ^{13}C NMR ($CDCl_3$) δ 157.5, 141.5, 130.0, 126.9, 125.6, 67.2, 53.7, 49.3, 41.7, 35.8, 31.4, 29.2, 28.0, 21.2; GC and HRMS, m/z (relative intensity) 287.22446(M^+, 38, calcd for $C_{19}H_{29}NO$ 287.22491), 272(71), 231(35), 190(3), 154(6), 148(8), 134(10), 130(22), 105(29), 91(36), 77(9), 58(100), 57(30).

2,2,7,7-Tetramethyl-3,6-diphenyl-4,5-bis(4,4,6-trimethyl-5,6-dihydro-1,3-oxazin-2-yl)octane (**156**)

Compound **156** was a liquid; ^{1}H NMR ($CDCl_3$) δ 7.37-6.93(m, 10H), 4.21-2.66(m, 4H), 1.32-0.65(m, 42H); GC and HRMS, m/z (relative intensity) 571.42609($M-1^+$, 10, calcd for $C_{38}H_{55}N_2O_2$ 571.42635), 557.41072($M-15^+$, 2, calcd for $C_{37}H_{53}N_2O_2$ 557.41070), 515(100), 376(2), 343(4), 331(4), 319(9), 236(6), 220(14), 192(9), 180(6), 131(39), 83(23), 58(34), 57(18).

General procedure for photostimulated alkylations of fumaronitrile and the derivatives of fumaronitrile in the presence of Dabco or PTSA

The substract (0.02-0.2 mmol), RHgX and coreactants were dissolved in 10 mL of deoxygeneated Me_2SO in a pyrex test tube

equipped with a rubber septrum. The mixture was irradiated under nitrogen by a 275-W General Electric sunlamp ca. 25 cm from the reaction tube. The reaction was quenched with aqueous sodium thiosulfate, neutralized and extracted with methylene chloride. The methylene chloride extract was washed three times with saturated aqueous sodium thiosulfate and once with brine solution, dried over Na_2SO_4, and the solvent evaporated. The ^1H NMR yield was determined with an internal standard (toluene) and if necessary, the products were isolated by flash column chromatography (silica gel) with hexane (95-99%) - ethyl acetate (1-5%). Some of the separated products were used as the starting material in other reactions (Tables 13 and 14).

2-Isopropylbutanedinitrile (**159**)[20]

Compound **159** had (lit.[20] decomposition 180-190 °C) ^1H NMR ($CDCl_3$) δ 2.89-2.65(m, 3H), 2.18-1.98(m, 1H), 1.13(d, *J*=6.6 Hz, 3H), 1.12(d, *J*=6.6 Hz, 3H); HRMS, m/z (relative intensity) 123.09221($M+1^+$, 0.7, calcd for $C_7H_{11}N_2$ 123.09222), 121.07625($M-1^+$, 1.2, calcd for $C_7H_9N_2$ 107.07657), 107(2), 94(2), 80(100); GCMS (CI, isobutane), m/z (relative intensity) 245($2M+1^+$, 2), 179(M+57, 90), 123(M+1, 100).

3-Cyano-4-methyl-3-pentenenitrile (**160**)

Compound **160** was a liquid that had ^1H NMR ($CDCl_3$) δ 3.31(s, 2H), 2.17(s, 3H), 1.98(s, 3H); ^{13}C NMR ($CDCl_3$) δ 159.0, 116.9, 115.2, 98.7, 24.8, 20.6, 18.7; GC and HRMS, m/z (relative intensity)

126.06866(M^+, 29, calcd for $C_7H_8N_2$ 126.06875), 105(8), 93(100), 80(13), 66(63), 43(51).

2,3-Diisopropylbutenedinitrile (**158**)

Compound **158** was a solid, mp 97-99 °C; ^1H NMR ($CDCl_3$) δ 3.10(septet, *J*=6.6 Hz, 1H), 1.22(d, *J*=6.6 Hz, 6H); GC and HRMS, m/z (relative intensity) 162.11536(M^+,11, calcd for $C_{10}H_{14}N_2$ 162.11570), 147(14), 132(6), 120(100), 105(9), 93(26), 82(21), 43(98).

N-Isopropyl derivative of isopropyl(3-cyano-2,4-dimethyl-3-pentyl)ketenimine(**161**)

Compound **161** was a liquid; FTIR at 2016 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.64(septet, *J*=6.6 Hz, 1H), 2.24(septet, *J*=6.6 Hz, 1H), 2.03(septet, *J*=6.6 Hz, 1H), 1.24(d, *J*=6.6 Hz, 6H), 1.15(d, *J*=6.6 Hz, 6H), 1.11(d, *J*=6.6 Hz, 6H), 1.03(d, *J*=6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 186.6, 120.9, 71.9, 55.3, 53.2, 34.3, 29.3, 23.8, 18.8, 17.8; GC and HRMS, m/z (relative intensity) 248.22521(M^+, 3, calcd for $C_{16}H_{28}N_2$ 248.22525), 233(2), 205(7), 163(100), 133(4), 121(18), 94(4), 67(4). Elemental analysis calculated for $C_{16}H_{28}N_2$: C, 77.36; H, 11.36; N, 11.28. Found: C, 77.38; H, 10.97; N, 11.45.

2-*tert*-Butylbutanedinitrile (**164**)[8]

Compound **164** was a solid, mp 89-89.5 °C (lit.[8] bp 420 K/0.2 mmHg); ^1H NMR ($CDCl_3$) δ 2.79-2.58(m, 3H), 1.12(s, 9H); GCMS, m/z (relative intensity) 135($M-1^+$, 0.1), 121(21), 94(28), 80(8), 67(17),

57(100), 53(11), 41(147).

2-*tert*-Butylbutenedinitrile (**162**)

Compound **162** was a solid, mp 119-119.5 °C; ^{1}H NMR ($CDCl_3$) δ 5.91(s, 1H), 1.27(s, 9H); ^{13}C NMR ($CDCl_3$) δ 146.3, 114.2, 109.1, 108.9, 37.3, 27.9; GC and HRMS, m/z (relative intensity) 134.08440(M^+, 3, calcd for $C_8H_{10}N_2$ 134.08440), 133.07671(M-1^+, 8, calcd for $C_8H_9N_2$ 137.07657), 119(100), 107(26), 107(30), 92(65), 76(11), 65(37), 57(57).

2,3-Di-*tert*-butylbutenedinitrile (**163**)

Compound **163** was a solid which had mp 85-86 °C; ^{1}H NMR ($CDCl_3$) δ 1.441(s); ^{13}C NMR ($CDCl_3$) δ 137.3, 115.9, 36.4, 29.6; GC and HRMS, m/z (relative intensity) 190.14679(M^+, 0.9, calcd for $C_{12}H_{18}N_2$ 190.14700), 175(5), 160(3), 145(1), 134(10), 119(3), 107(2), 95(11), 57(100).

2,3-Di-*tert*-butylbutanedinitrile (**165**)

Two diastereomers of compound **165** were isolated. One had mp 83-85 °C; ^{1}H NMR ($CDCl_3$) δ 2.64(s, 2H), 1.25(s, 18H); ^{13}C NMR ($CDCl_3$) δ 119.9, 41.6, 34.8, 27.6; GC and HRMS, m/z (relative intensity) 192.16208(M^+, 0.6, calcd for $C_{12}H_{20}N_2$ 192.16265), 191.15477(M-1^+, 3, calcd for $C_{12}H_{19}N_2$ 191.15482), 177(1), 161(0.8), 135(2), 121(6), 94(3), 82(7), 69(2), 57(100), 41(20); GCMS (CI, isobutane), m/z (relative intensity) 385(2M+1^+, 0.5), 249(M+57^+, 100), 193(M+1^+, 48).

The other diastereomer had mp 175-176 °C; ^{1}H NMR ($CDCl_3$) δ 2.57(s, 2H), 1.16(s, 18H); ^{13}C NMR ($CDCl_3$) δ 118.3, 41.6, 34.3, 27.4; GC and HRMS, m/z (relative intensity) 193.17095($M+1^+$, very small, calcd for $C_{12}H_{21}N_2$ 193.17047), 177.13906($M-15^+$, 1.5, calcd for $C_{11}H_{17}N_2$ 177.1393), 161(0.3), 135(2), 94(3), 80(3), 69(2), 57(100); GCMS (CI, isobutane), m/z (relative intensity) 385($2M+1^+$, 0.7), 249(M+57, 100), 193(M+1, 73).

2,N-Di-*tert*-butyl-3-cyano-4,4-dimethylpentanamide (**166**)

Compound **166** was isolated as two diastereomers. One had mp 212-216 °C; FTIR at 3354, 2233, 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.59(br, 1H), 2.53(d, *J*=1.8 Hz, 1H), 2.14(d, *J*=1.8 Hz, 1H), 1.37(s, 9H), 1.11(s, 9H), 1.09(s, 9H); ^{13}C NMR ($CDCl_3$) δ 169.6, 120.9, 54.5, 51.7, 41.1, 34.4, 33.7, 28.4, 28.3, 28.0; GC and HRMS, m/z (relative intensity) 266.23519(M^+, 1, calcd for $C_{16}H_{30}N_2O$ 266.23581), 251(4), 210(5), 194(8), 184(5), 166(4), 153(47), 128(8), 110(30), 97(21), 57(100). Elemental analysis calculated for $C_{16}H_{30}N_2O$: C, 72.13; H, 11.35; N, 10.51; O, 6.01. Found: C, 72.27; H, 11.08; N, 10.34. The other diastereomer had mp 168-173 °C; FTIR at 3373, 2233, 1672 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.19(br, 1H), 3.27(d, *J*=8.4 Hz, 1H), 1.93(d, *J*=8.4 Hz, 1H), 1.33(s, 9H), 1.20(s, 9H), 1.09(s, 9H); ^{13}C NMR ($CDCl_3$) δ 171.6, 122.7, 54.8, 51.8, 41.7, 34.6, 33.9, 28.7, 28.4, 27.7; GC and HRMS, m/z (relative intensity) 267.24409($M+1^+$, 2, calcd for $C_{16}H_{31}N_2O$ 267.24364), 251.21191($M-15^+$, 2, calcd for $C_{15}H_{27}N_2O$ 251.21234), 226(2), 209(12), 195(3), 184(33), 166(2), 153(69), 128(21), 110(16),

97(46), 57(100).

4-Cyano-2,2,5,5-tetramethyl-3-hexanone (**167**)

Compound **167** was a liquid; FTIR at 2237, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.740(s, 1H), 1.22(s, 9H), 1.16(s, 9H); ^{13}C NMR ($CDCl_3$) δ 206.0, 116.7, 46.4, 45.7, 35.2, 27.9, 26.1; GC and HRMS, m/z (relative intensity) 182.15461($M+1^{+}$, very small, calcd for $C_{11}H_{20}NO$ 182.15449), 181.14642(M^{+}, very small, calcd for $C_{11}H_{19}NO$ 181.14666), 153(0.5), 124(0.4), 97(3), 85(11), 57(100).

97(46), 57(100).

4-Cyano-2,2,5,5-tetramethyl-3-hexanone (**167**)

Compound **167** was a liquid; FTIR at 2237, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.740(s, 1H), 1.22(s, 9H), 1.16(s, 9H); ^{13}C NMR ($CDCl_3$) δ 206.0, 116.7, 46.4, 45.7, 35.2, 27.9, 26.1; GC and HRMS, m/z (relative intensity) 182.15461($M+1^+$, very small, calcd for $C_{11}H_{20}NO$ 182.15449), 181.14642(M^+, very small, calcd for $C_{11}H_{19}NO$ 181.14666), 153(0.5), 124(0.4), 97(3), 85(11), 57(100).

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GENERAL SUMMARY

The reactions of $Ph_2C=C(Y)NO_2$ (Y=SPh) with the anions of thiols and diethyl phosphite have been studied and the products formed rationalized in terms of mechanisms. Both anions yield products derived from an initially-formed Michael-type adduct. The nitro compounds can also be deoxygenated by the anion of diethyl phophite in Me_2SO at room temperature (Y=H, CH_3, SBu-*t*) or by triethyl phosphite at 150 °C (Y=H, CH_3, SPh, SBu-*t*, OPh) to generate azirines which rearrange to indoles via the nitrenes.

tert-Butylmercury halides in the presence of KI will photochemically deoxygenate nitro or nitrso compounds in a manner analogous to the reactions of Grignard reagents. Based on the reaciton products observed it is concluded that the reactions of *t*-BuHgI/KI with nitro compounds follows the scheme, $RNO_2 \longrightarrow RN(OBu\text{-}t)OHgI \longrightarrow RNO \longrightarrow RN(OBu\text{-}t)HgI \longrightarrow R\ddot{\underset{\cdot\cdot}{N}} \longrightarrow RN(Bu\text{-}t)HgI$.

Promotion of electron ttransfer by protonation of nitrogen-centered free radicals has been demonstrated to be a simple and useful method to improve the yield of the reductive alkylation products formed in the photochemical reaction of alkylmercury halides in the presence of iodide ion with substrates such α,β-unsaturated nitriles or imines derived from 1-azabutadiene.

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