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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

Ching-Fa Yao
Iowa State University

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Iowa State University, 1991
Deoxygenation reactions of 1-alkenyl nitro compounds with ethyl phosphites and alkylmercury iodides; Promotion of reactions of tertiary-butylmercury halides with α,β-unsaturated nitriles in the presence of proton donors

by

Ching-Fa Yao

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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\(_2\)C=C(SPh)NO\(_2\) in Me\(_2\)SO to form Ph\(_2\)C=C(SR) via conversion of the initial Michael-type adducts into Ph\(_2\)C(SR)CH=NO\(_2\)\(^-\) and Ph\(_2\)C=CHNO\(_2\)\(^-\).\(^4\) In a similar fashion, reaction of (EtO\(_2\))\(_2\)PO\(^-\) with Ph\(_2\)C=C(SPh)NO\(_2\) forms products from Ph\(_2\)C[PO(OEt)]CH(SPh)NO\(_2\) including Ph\(_2\)C[PO(OEt)]CH\(_2\)NO\(_2\), its Nef reaction product Ph\(_2\)C[PO(OEt)]CHO, or a Perkow-type reaction product Ph\(_2\)C[PO(OEt)]\(_2\)CN.\(^4\) However, reaction of Ph\(_2\)C=C(SPh)NO\(_2\) with (EtO\(_2\))\(_2\)PO\(^-\) 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\(_2\))\(_2\)PO\(^-\).

Similar results have been observed in the reaction Ph\(_2\)C=C(Y)NO\(_2\) (Y = H, CH\(_3\), NO\(_2\), SBu-\(t\)) and cis-\(\alpha\)-nitrostilbene with (EtO\(_2\))\(_2\)PO\(^-\). The deoxygenation of nitro and nitroso compounds to generate nitrenes
by tervalent phosphorous reagents has been previously reported.\textsuperscript{5} High yields of indoles or in one case an aziridine have been observed when Ph\textsubscript{2}C=C(Y)\textsubscript{N}O\textsubscript{2} reacted with (EtO)\textsubscript{3}P or (EtO)\textsubscript{2}POH at the temperature of 150 °C.\textsuperscript{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.\textsuperscript{6-14} The mixture of t-BuHgI and KI in Me\textsubscript{2}SO will reduce enolyl radicals to enolate anion\textsuperscript{15} in a process postulated to involve the ate-complex, t-BuHgI\textsubscript{2}.\textsuperscript{12} 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,

\begin{align*}
\text{Ar}_2\text{C}=\text{C}(\text{Y})\text{NO}_2 & \rightarrow \text{Ar}_2\text{C}=\text{C}(\text{Y})\text{N}(\text{OBu-t})\text{OHgI} \rightarrow \text{Ar}_2\text{C}=\text{C}(\text{Y})\text{NO} \rightarrow \\
\text{Ar}_2\text{C}=\text{C}(\text{Y})\text{N}(\text{OBu-t})\text{HgX} & \rightarrow \text{Ar}_2\text{C}=\text{C}(\text{Y})\text{N}^+ \rightarrow \text{Ar}_2\text{C}=\text{C}(\text{Y})\text{N}(\text{Bu-t})\text{HgI}. \quad (\text{Y}= \text{H, Me, Ph, SPh, SBu-t}).
\end{align*}

The photostimulated addition of alkylmercury chlorides to substituted ethylenes has been studied by Russell et al.\textsuperscript{16} α,β-Unsaturated nitriles and 2-(1-alkenyl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazines react with alkylmercury halides 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 \( \alpha \)-phenyl-\( \beta \)-nitrostyrenes with the anions of thiols and diethyl phosphite; Formation of indoles by reaction with ethyl phosphites

Ching-Fa Yao and Glen A. Russell

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Reactions of excess RS\(^-\) (R=Ph, \(t\)-Bu) with Ph\(_2\)C=C(SPh)NO\(_2\) in Me\(_2\)SO form Ph\(_2\)C=CHSR via conversion of the initial Michael-type adducts into Ph\(_2\)C(SR)CH=NO\(_2\)\(^-\) and Ph\(_2\)C=CHNO\(_2\)\(^-\). In a similar fashion, reaction of (EtO)\(_2\)PO\(^-\) with Ph\(_2\)C=C(SPh)NO\(_2\) forms initially PhSP(O)(OEt)\(_2\) and Ph\(_2\)C[P(O)(OEt)\(_2\)]CH=NO\(_2\)\(^-\) which upon acidic work-up will yield the nitroalkane or the Nef reaction product, Ph\(_2\)C[P(O)(OEt)\(_2\)]CHO. The reaction of (EtO)\(_2\)PO\(^-\) with Ph\(_2\)C=C(SPh)NO\(_2\) also produces Ph\(_2\)C[P(O)(OEt)\(_2\)]CN via a Perkow-type reaction of the Michael adduct to yield, Ph\(_2\)C[P(O)(OEt)\(_2\)]CH=N(O)OP(O)(OEt)\(_2\) as an intermediate. The nitrile is also formed from Ph\(_2\)C[P(O)(OEt)\(_2\)]CH(NO\(_2\))\(_2\) with (EtO)\(_2\)PO\(^-\) in (EtO)\(_2\)P(O)H or Me\(_2\)SO at 30 °C and in >95% yield by the reaction of (EtO)\(_3\)P with Ph\(_2\)C[P(O)(OEt)\(_2\)]CH(NO\(_2\))\(_2\) at 150 °C. Reaction of Ph\(_2\)C=C(R)NO\(_2\) (R=H, CH\(_3\)) or Ph\(_2\)C[P(O)(OEt)\(_2\)]CH\(_2\)NO\(_2\) with excess (EtO)\(_2\)PO\(^-\) in Me\(_2\)SO or (EtO)\(_2\)P(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\(_2\)C=C(R)N(O\(^-\))OP(O)(OEt)\(_2\), Ph\(_2\)C=C(R)NOP(O)(OEt)\(_2\)\(^-\) and 2,2-diphenyl-2\(H\)-azirine or 2,2-diphenyl-3-methyl-2\(H\)-azirine. Similarly, Ph\(_2\)C=C(SBu-\(t\))NO\(_2\) and (EtO)\(_2\)PO\(^-\) give 3-(\(t\)ert-butylthiyl)-2,2-diphenyl-2\(H\)-azirine in Me\(_2\)SO or 2-(\(t\)ert-butylthiyl)-3-phenylindole in (EtO)\(_2\)P(O)H solution. Reaction of (\(E\))-PhHC=C(Ph)NO\(_2\) (cis-\(\alpha\)-nitrostilbene) with (EtO)\(_2\)PO\(^-\) in Me\(_2\)SO 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 Ph₂C=CH(X)NO₂ 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 Ph₂C=CN₃NO₂ in (EtO)₂P(O)H at 150 °C. Reaction of (E)-PhHC=C(Ph)NO₂ 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)$_2$P(O)$^-$ (P$^-$) in Me$_2$SO gives upon acidification a quantitative yield of the adduct 2d. The adduct 2a is also formed from 2-nitro-1,1-diphenylethylene with P$^-$ in the presence of (EtO)$_2$P(O)H (PH). However, reaction of one equiv of RS$^-$ with 1d in Me$_2$SO lead to the displacement of a nitro group forming 1b or 1c in high yield while 1a is converted to Ph$_2$C=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$_2$C=CHPh 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

\[
\begin{align*}
3 + RS^- &\longrightarrow RSSPh + Ph_2C(SR)CH=NO_2^- \\
RS^- + 1a &\longrightarrow Ph_2C=CHSR^a + NO_2^- \\
\end{align*}
\]

\textsuperscript{a}The possibility exists that Ph$_2$C(SPh)CH=NO$_2^-$ might be converted into Ph$_2$C=CHPh + NO$_2^-$ in an intramolecular reaction.\textsuperscript{1}
In a similar fashion, the reaction of $P^-$ with $1b$ initially forms mainly $2a$ and $\text{PhSP(O)(OEt)}_2$ via nucleophilic attack upon the sulfur atom in the adduct $2b$. However, we found that the reactions of excess $P^-$ with the $\alpha$-phenyl-$\beta$-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 $(\text{EtO})_3\text{P}$ 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$^b$ $4a$-$f$. While $6d$ is formed from $1d$ in $(\text{EtO})_2\text{P(O)}_\text{H}$.  

\[ \begin{align*}
(1) & \quad \text{Ph}_2\text{C} = \text{C}(X)\text{NO}_2 \\
(2) & \quad \text{Ph}_2\text{C}[\text{P(O)(OEt)}_2]\text{CH}(X)\text{NO}_2 \\
(3) & \quad \text{Ph}_2\text{C}(\text{SR})\text{CH(SPh)}\text{NO}_2 \\
1a & \quad X=\text{H} \\
1b & \quad X=\text{PhS} \\
1c & \quad X=\text{t-BuS} \\
1d & \quad X=\text{NO}_2 \\
1e & \quad X=\text{CH}_3 \\
1f & \quad X=\text{PhO} \\
2a & \quad X=\text{H} \\
2b & \quad X=\text{PhS} \\
2c & \quad X=\text{t-BuS} \\
2d & \quad X=\text{NO}_2 \\
3a & \quad R=\text{Ph} \\
3b & \quad R=\text{t-Bu} \\
\end{align*} \]

$^b$The thermal conversion of $2H$-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 $2H$-azirines.$^6,7$
cis-α-Nitrostilbene also leads to indoles \( \textbf{8a-c} \) and compound \( \textbf{2} \) under these conditions in Me\(_2\)SO or EtOH. The formation of 2-alkyl-3-(diethoxyphosphinyl)-N-hydroxyindoles (analogous to \( \textbf{8c} \)) has been previously reported for the reaction of PhCH=\( \text{C(R)NO}_2 \) with (EtO)\(_2\)P(0)H/K\(_2\)CO\(_3\) in EtOH.\(^8\) The formation of the indole \( \textbf{8a} \) from (\( E \))-PhCH=\( \text{C(Ph)NO}_2 \) has also been reported to occur upon deoxygenation with (EtO)\(_3\)P.\(^9\)

\[ \textbf{4} \quad \text{Ph} \quad \text{C} \quad \text{C} \quad \text{N} \quad \text{X} \]

\[ \textbf{5} \quad \text{Ph} \quad \text{C} \quad \text{C} \quad \text{N} \quad \text{P(O)(OEt)}_2 \]

\[ \textbf{6} \quad \text{Ph} \quad \text{N} \quad \text{H} \quad \text{X} \]

\[ \begin{array}{cccc}
\textbf{4a} & X=H & \textbf{5a} & X=H \\
\textbf{4b} & X=\text{PhS} & \textbf{5b} & X=\text{CH}_3 \\
\textbf{4c} & X=t-\text{Bus} & \textbf{5c} & X=t-\text{Bus} \\
\textbf{4d} & X=\text{NO}_2 & \textbf{5d} & X=\text{NO}_2 \\
\textbf{4e} & X=\text{CH}_3 & \textbf{5e} & X=\text{CH}_3 \\
\textbf{4f} & X=\text{PhO} & \textbf{5f} & X=\text{PhO} \\
\end{array} \]

β-Nitrostyrene does not form indole\(^c\) under these conditions\(^{10,11}\) and at ambient temperatures yield products derived from the addition of (EtO)\(_3\)P at the alpha carbon atom,\(^{12}\) a process apparently hindered by an α-phenyl substituent.

\(^c\)Pyrolysis of 2-phenyl-2\(H\)-azirine forms PhCH\(_2\)CN and indole in approximately equal amounts.\(^{4,11}\)
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. 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

\[
\begin{align*}
\text{Scheme III}
\end{align*}
\]
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 Me2SO to form Ph2C=CHSPh (94% isolated yield) and PhSSPh or with excess t-BuS- to form Ph2C=CHSBu-t (88% isolated yield). The reactions are neither stimulated by sunlamp irradiation nor retarded by 5-10% of (t-Bu)2NO- or p-O2NC6H4NO2. The only effect of exposure to air is an increased yield of PhSSPh. It thus appears that the reaction of 1b with RS- in Me2SO is an ionic process. Furthermore, in the early stages of the reaction, Ph2C=CHNO2 can be detected as intermediate (Fig. 1). This supports the process of Scheme I (R=Ph or t-Bu). The nitro-substitution product [Ph2C=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 [Ph2C(SPh)CH(SBu-t)NO2] may not be formed, or if formed at a low equilibrium concentration, the adduct may be stericly hindered to nucleophilic attack by PhS-. The adduct 3a could not be detected by GCMS in the CH2Cl2 extracts of the hydrolysis products from the reaction of 1b with a deficiency of PhSK/PhSH in Me2SO, THF, DMF or EtOH. In Me2SO 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 Me₂SO at 25 °C; O, % Ph₂C=CH₂SPh; ●, % Ph₂C=CHNO₂
The reaction of 5 equiv. of P⁻ with 1b in Me₂SO 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 Me₂SO 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 Ph₂C[P(O)(OEt)₂]CHO expected from Ph₂C[P(O)(OEt)₂]CH=NO₂H.

Minor products observed in the reaction of 1b with P⁻ in Me₂SO include 1a, 7a, PhSSPh, the indole 6b and at longer reaction times the indole 6a. In moist Me₂SO, Ph₂CO is formed from the hydrolysis of 1b with traces of Ph₂C(NH₂)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 Ph₂C(NH₂)COOEt).

Reactions leading to Ph₂C[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$_2$C=C(SPh)NO$_2$ ($\textbf{1b}$) with (EtO)$_2$POK in Me$_2$SO at 25-30 °C

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

$^a$By GC using biphenyl as an internal standard.

$^b$7a (tr), 6b (tr), Ph$_2$S$_2$ (7%), Ph$_2$C=CHSPh (6%), 1a (2%).

$^c$7a (tr), 6b (tr), Ph$_2$S$_2$ (4%), Ph$_2$C=CHSPh (6%), 1a (3%).

$^d$7a (tr), 6b (tr), Ph$_2$S$_2$ (4%), Ph$_2$C=CHSPh (8%), 1a (3%).

$^e$Isolated by column chromatography.
elimination of \((\text{EtO})_2\text{PO}_2\text{H}\)\(^{15,d}\) (Scheme IV, \(X=\text{PhS}\)). There are several literature precedents for such reactions of \(\alpha\)-substituted nitroalkanes.

Scheme IV

\[
\begin{align*}
2 + P^- & \rightarrow \text{Ph}_2\text{C}[\text{P}(\text{O})(\text{OEt})_2]\text{CH}(X)\text{N}(O^-)\text{OP}(O)(\text{OEt})_2 \\
\rightarrow & \ X^- + \text{Ph}_2\text{C}[\text{P}(\text{O})(\text{OEt})_2]\text{CH=N}(O)\text{OP}(O)(\text{OEt})_2 \\
\frac{10}{-[O]} & \rightarrow \frac{7\_d}{-(\text{EtO})_2\text{PO}_2\text{H}}
\end{align*}
\]

\(^d\)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 \((\text{EtO})_3\text{P}\). Although the conversion of a nitro group to a nitroso group can be readily rationalized from \(ii\) or \(iii\), the Perkow reaction of \(2\_b\) or \(2\_d\) and azirine formation from \(1\), is much better accommodated by \(iii\) and the analogous deoxygenated species \(-\text{NOP}(O)(\text{OEt})_2^-\).
with phosphorus nucleophiles. Thus reaction 1 occurs readily, and the same product is formed

\[
\text{Me}_2\text{C(NO}_2\text{)}_2 + \text{P}^- \xrightarrow{\text{Me}_2\text{SO}} \text{[Me}_2\text{C=NO(OOP(O(OEt))}_2\text{]} - [\text{O}] \xrightarrow{} \text{Me}_2\text{C=NOO(OOP(O(OEt))}_2\text{] (1)}
\]

from the Perkow/Arbuzov reaction of (EtO)_3P with Me_2C(Cl)NO_2. 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 (EtO)_2PCl, the timing of the deoxygenation and elimination steps is not clear since an E2 elimination from (EtO)_2PCl would produce a nitrile oxide [Ph_2C[P(O)(OEt)_2CN(O)] which would be readily deoxygenated to the nitrile. 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)(OOP(OEt))_2 rearranges to PhCH=CNO(OOP(OEt))_2 which eliminates (EtO)_2PO_2H. Reaction of Me_2C=NO_2^- with (EtO)_2PCl yields Me_2C=NOO(OOP(OEt))_2.

Reactions of Ph_3P with α-substituted 2º-nitroalkanes also occur 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=NOOPPh_3^+ which after
deoxygenation reacts with Ph₃P to form Ph₃P=C(Ar)CN and a 2H-azirine which can methanolized to PhC(OMe)=NCH₂PPh₃Br⁻. ³¹

The reaction of 2d with 5-10 equiv of P⁻ also forms the nitrile 7d in Me₂SO or PH solution. However, the nitrile is now accompanied by an equal amount of Ph₂CHP(O)(OEt)₂. Both products can be explained by Scheme IV (with X=NO₂) if elimination of NO₂⁻ and Ph₂CP(O)(OEt)₂⁻ are competitive. (With the better leaving group PhS the elimination of Ph₂CP(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, Ph₂C[P(O)(OEt)₂]CNO (fragmentation forms Ph₂CCNO⁺ 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=NO₂ and (EtO)₃P in place of P⁻. If this is so, only NO₂⁻ is eliminated from the intermediate Ph₂C[P(O)(OEt)₂]CH(NO₂)N(O⁻)OP(OEt)₃⁻, possibly because of an interaction between the nitro oxygen atom and the positively charged phosphorus atom.

Nitroalkanes such as PhCH₂CH₂NO₂ 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 Ph₂C[P(0)(OE)₂]CH₂NO₂ (2a) or Ph₂C[P(0)(OE)₂]CH(NO₂)₂ (2d) in ethyl phosphite solution at 150 °C

<table>
<thead>
<tr>
<th>Substrateᵃ</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Product (%)ᵇ</th>
<th>7d</th>
<th>Ph₂CHP(O)(OE)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>2d</td>
<td>(EtO)₃P</td>
<td>1</td>
<td>&gt;95</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>(EtO)₃P/(EtO)₂P(O)Hᵈ</td>
<td>1</td>
<td>&gt;95</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>(EtO)₂P(O)H</td>
<td>1</td>
<td>14</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>(EtO)₃P</td>
<td>1</td>
<td>23</td>
<td>26ᵉ</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>(EtO)₃P/(EtO)₂P(O)Hᵈ</td>
<td>1</td>
<td>22</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>(EtO)₂P(O)H</td>
<td>1</td>
<td>32</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>(EtO)₂P(O)H</td>
<td>13</td>
<td>14</td>
<td>19</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ0.3 mmol of substrate in 1 mL of the phosphite.
ᵇBy GC using biphenyl as an internal standard.
ᶜNot observed.
ᵈ1:1 volume ratio (3.9 mmol of (EtO)₂P(O)H and 2.9 mmol of (EtO)₃P).
ᵉ7% of 5a observed.
considerable amounts of Ph₂CHP(O)(OEt)₂ in addition to 7d, presumably from the elimination of Ph₂CP(O)(OEt)₂⁻ from the intermediate Ph₂C[P(O)(OEt)₂]CH₂N(O⁻)OP(OEt)₃⁺. Table 2 also presents evidence that suggest that 7d can be slowly converted to Ph₂CHP(O)(OEt)₂ by reaction with PH at 150 °C (compare entries 6 and 7).

**Conversion of Ph₂C=C(X)NO₂ into 2H-azirines and 2-X-3-phenylindoles**

The reaction of one equiv of P⁻ with Ph₂C=CHNO₂ establishes an equilibrium with 2a. With 1a=0.5 M, hydrolysis gave 2a in 7% yield after 144h in Me₂SO or in 37% after 1h in PH. In PH solution 2a was accompanied by significant amount of the aziridine 5a. With excess P⁻ in Me₂SO or PH, the aziridine is the major product from either Ph₂C=CHNO₂ 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 Me₂SO 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 Me₂SO, the aziridine 5b (51%) is the major product formed from 1e (Ph₂C=C(CH₃)NO₂) in 2 h. Support for the mechanism of Scheme V was provided by the observation that in Me₂SO the major
product formed from \textbf{1c} and excess \textit{P} \textsuperscript{−} was the azirine \textbf{4c} (Reaction 2). Compound \textbf{4c} was isolated in 49% yield (plus 9% of the hydrolysis product Ph\textsubscript{2}C(OH)C(SBu-\textit{t})=NH) after a 2 h reaction period in Me\textsubscript{2}SO following the dropwise addition of \textbf{1c} to 10 equiv. of 0.25 M \textit{P} \textsuperscript{−}. Also

\textbf{Scheme V}

\[ \begin{align*}
1 + \textit{P} \textsuperscript{−} & \rightarrow \text{Ph}_2\text{C}=\text{C}(X)\text{N}(\textit{O}^{−})\text{OP}(\text{O})(\text{OEt})_2 \\
& \rightarrow (\text{EtO})_2\text{PO}_2^{−} + \text{Ph}_2\text{C}=\text{C}(X)\text{N}=\text{O} \quad \text{P} \textsuperscript{−} \\
\text{Ph}_2\text{C}=\text{C}(\text{SBu-\textit{t}})\text{N}0_2 + \textit{P} \textsuperscript{−} & \rightarrow 4 + (\text{EtO})_2\text{PO}_2^{−} \\
\text{Ph}_2\text{C}=\text{C}(\text{SBu-\textit{t}})\text{NO}_2 + \textit{P} \textsuperscript{−} & \rightarrow \text{Ph}_2\text{C}=\text{C}(\text{SBu-\textit{t}})\text{N}0_2 \quad \text{Me}_2\text{SO} \\
\end{align*} \]

observed were traces of Ph\textsubscript{2}CHCN(\textbf{7a}) and \textit{t}-BuSP(O)(OEt)\textsubscript{2}. In PH as solvent \textbf{4c} appeared to be the major initial product (by GC) but it was rapidly converted into a 7:1 mixture of the indole \textbf{6c} and the nitrile \textbf{7c}, Scheme VI. The indole was isolated in 53% yield from a 30 min reaction of \textbf{1c} with 5 equiv of \textit{P} \textsuperscript{−} in PH. In this reaction after 2 min, GC analysis indicated a ratio of \textbf{4c}:\textbf{6c} of ~5:1 but after 30 min, \textbf{4c} was not detected. The nitrile \textbf{7a} and a trace of \textit{t}-BuSP(O)(OEt)\textsubscript{2} were also observed but the yield of \textbf{7a} did not increase after the initial 30 min
reaction period. In this case, 7a in not formed by nucleophilic attack upon 7c.

Scheme VI

\[
\begin{align*}
4c & \xrightarrow{H^+} \text{Ph}_2\text{C}C(\text{SBu-t})\text{NH}^+ \\
& \xrightarrow{\text{Ph}_2\text{C}(\text{SBu-t})\text{C}==\text{NH}^+} 7c \\
& \xrightarrow{\text{SBu-t}^+} 6c
\end{align*}
\]

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 equilibrium 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.

\(^e\)Alternatively, Scheme V, with X=H could be entered by rearrangement of Ph2C[P(O)(OEt)2]CH=NO2\(^-\) to Ph2C=CHN(O\(^-\))OP(O)(OEt)2. Reactions which form 2a in low yield, e.g. [P\(^-\)]=[1a]=0.05 M in Me2SO, 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-2H-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 Ph2CHCN (e.g. Ph2CHC(O)SBu-t, Ph2CHC(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 Me2SO or PH is unclear. Rearrangement with elimination of (EtO)2PO2- from 11 (X=PhS) to form 7b which could be the precursor to 7a is a possibility 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)2PO2.
Table 3. Reactions of Ph$_2$C=C(X)NO$_2$ with ethyl phosphites at 150 °C

<table>
<thead>
<tr>
<th>X$^a$</th>
<th>Phosphite$^b$</th>
<th>Time(h)</th>
<th>Products$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>(EtO)$_3$P</td>
<td>1</td>
<td>6a (73%), 5a (12%)</td>
</tr>
<tr>
<td>H</td>
<td>(EtO)$_3$P</td>
<td>24</td>
<td>6a (69%), 5a (14%)</td>
</tr>
<tr>
<td>H</td>
<td>(EtO)$_3$P/(EtO)$_2$P(O)H (4:1)</td>
<td>24</td>
<td>6a (96%)</td>
</tr>
<tr>
<td>H</td>
<td>(EtO)$_3$P</td>
<td>24$^d$</td>
<td>6a (90%)$^e$</td>
</tr>
<tr>
<td>H</td>
<td>(EtO)$_3$P/EtOH (1:9) (95 °C)</td>
<td>5h</td>
<td>6a (57%), 2a (25%), 5a (5%), 1a (10%)</td>
</tr>
<tr>
<td>PhS</td>
<td>(EtO)$_3$P</td>
<td>0.5</td>
<td>6b (99%)$^e$</td>
</tr>
<tr>
<td>t-BuS</td>
<td>(EtO)$_3$P</td>
<td>1</td>
<td>6c (95%)$^e$</td>
</tr>
<tr>
<td>t-BuS</td>
<td>(EtO)$_2$P(O)H</td>
<td>4.4</td>
<td>6c (25%)$^e$, 2-(ethylthiyl)-3-phenylindole (16%)$^e$, Ph$_2$CHP(O)(OEt)$_2$(10%), Ph$_2$CHC(O)S-Bu-t (6%)$^e$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>(EtO)$_2$P(O)H</td>
<td>0.5</td>
<td>6a (52%), 6a (3%), 1a (2%), 1d (12%)</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>(EtO)$_2$P(O)H</td>
<td>3</td>
<td>6d (19%)$^e$, 6a (6%)$^e$, Ph$_2$CHP(O)(OEt)$_2$ (15%)$^e$</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>(EtO)$_3$P</td>
<td>1</td>
<td>6e (100%)</td>
</tr>
<tr>
<td>PhO</td>
<td>(EtO)$_3$P</td>
<td>2</td>
<td>6f (89%)$^f$</td>
</tr>
</tbody>
</table>

$^a$0.3-1 mmol of Ph$_2$C=C(X)NO$_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 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\textsubscript{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\textsuperscript{-} and 5 equiv of PH with (E)-PhCH=C(Ph)NO\textsubscript{2} forms diethyl(2-nitro-1,2-diphenylethyl)phosphonate in Me\textsubscript{2}SO at 25 °C. In EtOH the P\textsuperscript{-} generated from 1 equiv of PH and 5 equiv of K\textsubscript{2}CO\textsubscript{3}, reacted with cis-α-nitrostilbene at 70 °C in 10 h to form 8\textsubscript{b} (14%) and 8\textsubscript{c} (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\textsuperscript{-} is required to form the N-hydroxyindole 8\textsubscript{c} whereas two equivalents of P\textsuperscript{-} are required to form the indole 8\textsubscript{b}.

Reaction of cis-α-nitrostilbene with (EtO)\textsubscript{3}P for 3 h at 150 °C produced compound 2 in 77% yield. A trace of 2-phenylindole was also produced. A possible mechanism for the formation of 2 is given in Scheme VIII. It is not obvious why a ketenimine is formed from PhCH=C(Ph)\textsubscript{N} and not from Ph\textsubscript{2}C=C(X)\textsubscript{N} with X=H, Ph, CH\textsubscript{3}, SPh or t-BuS. One possibility is that PhCH=C(Ph)\textsubscript{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

(P(O)(OEt)_2)_2 Ph —C NO2 Ph

P'/PH

(P(O)(OEt)_2)_2 Ph —C =N02H

Ph —C(Ph) —N=0

H^+

P(O)(OEt)_2 Ph —C=C(Ph)

P(O)(OEt)_2 Ph —C(Ph)

12

13

14

15

8c

8b

-(EtO)_3PO
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-2H-azirines 4b-4f, some of the aziridine 5a was formed from 1a under this condition, presumably via 2,2-diphenyl-2H-azirine 4a.
Reaction of ethyl phosphites with β-nitrostyrene

Formation of the 2H-azirine from β-nitrostyrene should lead to PhCH₂CN and indole.⁴,¹¹ In a previous study of the reaction of (RO)₃P (neat, DME, t-BuOH) with PhCH=CHNO₂ at room temperature, PhC[P(O)(OR)₂]=CH₂, PhCH[P(O)(OR)₂]CH₂NO₂ 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=CHNO₂ with P⁻ at 25-35 °C and with (EtO)₃P or (EtO)₂POH at 150 °C. However, indole or PhCH₂CN were not observed.

With 1 equiv of P⁻ in PH, PhCH[P(O)(OEt)₂]CH₂NO₂ was formed slowly at room temperature (10% in 12 h) while with excess P⁻ the major product was PhCH[P(O)(OEt)₂]CH₂P(O)(OEt)₂. Reaction of PhCH=CHNO₂ 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]=CH₂ (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]=CH₂ (10%) and trace of PhCH[P(O)(OEt)₂]CH₂[P(O)(OEt)₂] was formed.

The formation of PhC[P(O)(OEt)₂]=CH₂ and the diphosphonate undoubtedly involves the elimination of HNO₂ from PhCH[P(O)(OEt)₂]CH₂NO₂. A similar process forming the diphosphonate via PhCH[P(O)(OEt)₂]=CH₂ from PhCH=CHSO₂Ph and P⁻ in Me₂SO has been recently described.²⁰ The reaction of PhCH=CHNO₂
with PH at 150 °C apparently involves the initial formation of PhCH[P(O)(OEt)2]CH2NO2 which can undergo either the loss of HNO2 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

![Diagram](image)

PhCH[P(OEt)3+]CH=NO2 or PhCH=CHN(O-)OP(OEt)3+.12 The contrasting behaviors of PhCH=CHNO2 or PhCH=C(Ph)NO2 and Ph2C=CHNO2 with P(III) reagents are a consequence of the presence of the ionizable α-hydrogen atom in the adducts formed from PhCH=CHNO2 or PhCH=C(Ph)NO2.

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. A short summary of the formulation by Hassner is given in Scheme IX.

Scheme IX

\[ R' \xrightarrow{-N_2, \text{concerted}} R'' \]

\[ R = \text{O-C}_6\text{H}_4-\text{CH}_3 \]

\[ R' = \text{Ph} \]

\[ R' = o-\text{C}_6\text{H}_5-\text{CH}_3 \]
CONCLUSION

The reactions of RS\(^-\) with Ph\(_2\)C=C(SPh)NO\(_2\) to form Ph\(_2\)C=CHSR have been identified as involving nucleophilic attack upon in the initially-formed Michael-type adducts. The reaction intermediate Ph\(_2\)C=CHNO\(_2\) has been detected during the reaction. The anion (EtO)\(_2\)PO\(^-\) can undergo Michael-type addition to Ph\(_2\)C=C(SPh)NO\(_2\) to yield products derived from Ph\(_2\)C[P(O)(OEt)\(_2\)]CH(SPh)NO\(_2\) such as Ph\(_2\)C[P(O)(OEt)\(_2\)]CH\(_2\)NO\(_2\), Ph\(_2\)C[P(O)(OEt)\(_2\)]CHO and Ph\(_2\)C[P(O)(OEt)\(_2\)]CN. Deoxygenation of Ph\(_2\)C=C(Y)NO\(_2\) by (EtO)\(_2\)PO\(^-\) in Me\(_2\)SO at room temperature also yields azirines which can be isolated in the case of Y=t-BuS or trapped by addition of (EtO)\(_2\)PO\(^-\) to yield an aziridine in the case of Y=H or CH\(_3\). At 150 °C (EtO)\(_3\)P reacts with Ph\(_2\)C=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 spectra 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 apparatus 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)$_3$P, (EtO)$_2$P(O)H, PhSH, $t$-BuSH,
PhCH=CHNO₂, t-BuOK and Ph₂C=CH₂ 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 N₂.

Reactants prepared according to literature procedures were 1a, 1b, 1c, 1d, 1e, 1f, 2d and (E)PhCH=C(Ph)NO₂. The following reaction products were either prepared according to literature procedures or had physical and spectroscopic properties in agreement with literature values: Ph₂C=C(SPh)₂, Ph₂CH[P(0)(0Et)₂], PhSP(O)(OE), CH₂(NO₂), PhC[P(O)(0Et)₂]CH₂P(O)(0Et)₂, 3-phenylindole, l,1-diphenyl-2,2-bis(phenylthiyl)ethylene, 2-methyl-3-phenylindole.

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 C₁₈H₂₀N₂O₇PK (elemental Anal. C, H, N), mp 133-135 °C; ¹H NMR (Me₂SO-δ 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; ¹H NMR (CDCl₃) δ 7.68(d, JₚH=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 (Cl, 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 Ph₂C=CHNO₂ (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 CH₂Cl₂. 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; ¹H NMR (CDCl₃) 7.55-7.32(m, 10H), 5.46(d, JₚH=9.0 Hz, 2H), 3.94-3.84(m, 2H), 3.78-3.68(m, 2H), 1.16(t, J=7.2 Hz, 6H); ¹³C NMR (CDCl₃) δ 136.1(d, JₚC=7.2 Hz), 129.7(JₚC=1.6 Hz), 127.9, 127.7, 78.7, 63.9(d, JₚC=7.0 Hz), 55.6(d, JₚC=132 Hz), 16.1(d, JₚC=5.0 Hz). GC and HRMS, m/z (relative intensity) 363.1246(M⁺, 2, calcd for C₁₈H₂₂NO₅P 363.1236), 317.1304(M⁺-NO₂, 27, calcd for C₁₈H₁₉O₃P 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 Me₂SO was added dropwise to a solution of 4.75 mmol each of PhSH and t-BuOK in 10
mL of Me₂SO. After stirring for 30 h under N₂ 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 Ph₂C=CHSPh whose spectra and GC retention time agreed with an independently 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 Me₂SO containing biphenyl (1 mmol) 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 Ph₂C=CHSPh, 0.3% of Ph₂C=CHNO₂ and a 1.3 mmol of PhSSPh. In Me₂SO which had not been thoroughly dried, appreciable quantities of Ph₂C=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⁺-Ph₂S₂, 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 Ph₂C=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 Me2SO and stirred for 23 h under N2. The product was hydrolyzed with brine, extracted by CH2Cl2 and the filtrate dried over Na2SO4. Using toluene as an internal standard the 1H NMR yield of Ph2C=CHSBu-t was 88%. Material isolated by column chromatography with hexane had mp 56-58 °C; 1H NMR (CDCl3) δ 7.40-7.18(m, 1OH), 6.77(s, 1H), 1.43(s, 9H); GC and HRMS, m/z (relative intensity) 270(2.7), 268.12846(M+, 42, calcd for C18H20S 268.12858), 212(100), 178(20), 165(12), 77(6), 57(28).

g-(Diethoxyphosphinyldiphenylacetaldehyde

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 CH2Cl2. 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 (CDCl3) δ 9.93(d, JPH= 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 C18H21O4P 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-(Diethoxyphosphinyldiphenylacetonitrile (7d)

Addition of 2 (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 (CDCl₃) 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); ¹³C NMR (CDCl₃) δ 134.2(d, JPC=4.4 Hz), 128.8, 128.6, 128.5, 118.8(d, JPC=12.6 Hz), 65.1(d, JPC=7.1 Hz), 52.9(d, JPC=137 Hz), 16.2(d, JPC=4.1 Hz); FTIR at 2250 cm⁻¹; GC and HRMS, m/z (relative intensity) 329.1179(M⁺, 70, calcd for C₁₈H₂₀NO₃P, 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%), Ph₂CHP(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 Ph₂CHP(O)(OEt)₂ (8%) while a 13 h reaction period gave only 14% of 7d and 19% of Ph₂CHP(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 Ph₂CHP(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 CH₂Cl₂. 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 (CDCl₃) 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); ¹³C NMR (CDCl₃) δ 143.6(d, JPC=0.9 Hz), 138.4(d, JPC=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, JPOC=7.1 Hz), 61.9(d, JPOC=6.0 Hz), 49.4(d, JPC=2.6 Hz), 38.5(d, JPC=199 Hz), 16.1(d, JPC=6.6 Hz), 16.0(d, JPC=6.0 Hz). The assignment of JPC and δ for the diastereotopic carbons of the ethoxy groups was established by comparison of the 75 and 125 MHz proton-decoupled ¹³C 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 3JPH 7.2 Hz). The methine hydrogen at δ 2.70 is not coupled to any other hydrogen atom.
therefore is coupled to phosphorous, $^{2}J_{PH}=16.5$ Hz (coupling to the methine $^{13}$C is 164 Hz). The $^{31}$P NMR spectrum is at $\delta 20.94$ (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$_{3}$P 331.13374), 330.1254(M-1+, 6; calcd for C$_{18}$H$_{21}$NO$_{3}$P 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$_{7}$H$_{7}^{+}$ 91.05478).

**Reaction of 1b with (EtO)$_2$PO$^{-}$**

With excess P$^-$ (10 equiv.) in dry Me$_2$SO 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$_2$Cl$_2$ and analysis by GC and GCMS. At lower P/$^{1}$a ratios or in the presence of (EtO)$_2$P(O)H, the yield of the indole 6a increased. In moist Me$_2$SO, Ph$_2$C=O (and products derived from Ph$_2$C=O) are formed from the hydrolysis of 1b. In one experiment with 2 equiv of P$^-$ in moist Me$_2$SO the ethyl ester of $\alpha$-aminodiphenylacetic acid [Ph$_2$C(NH$_2$)CO$_2$Et] was isolated by column chromatography; $^{1}$H NMR (Me$_2$SO-d$_6$) $\delta$ 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 2sL (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, Ph2CHP(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
Ph2CHP(O)(OEt)2.

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

The nitroalkene 1c (1.2 mmol) in 25 mL of Me₂SO was added
dropwise to a mixture of (EtO)₂P(O)H (12 mmol) and t-BuOK (12
mmol) in 25 mL of Me₂SO 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 CH₂Cl₂ and the extract washed, dried
over Na₂SO₄ and concentrated to an oily residue. Flash column
chromatography using hexane (99%) - ethyl acetate (1%) gave a
product which was separated by TLC into 4c (49%) and 9% of a
hydrolysis product. The azirine 4c had mp 69-72 °C; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.70-7.20 (m, 10H), 1.67 (s, 9H); FTIR (CH\(_2\)Cl\(_2\)) 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 \(\delta\) 9.63 with other absorption at \(\delta\) 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 structure, Ph\(_2\)C(OH)C(SBu-t)\(=\)NH, rather than the oxime Ph\(_2\)C(SBu-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\(_2\)CHO\(^+\)), C\(_{13}\)H\(_{11}\)O\(^+\)(Ph\(_2\)CHO\(^+\)) and C\(_7\)H\(_5\)O\(^+\)(PhCO\(^+\)), respectively and no fragments containing sulfur and/or nitrogen come close to the observed values of m/z (e.g. PhCH=NH\(^+\) is 160 ppm lower than the mass measured for the 105 peak). The structure thus requires the unit Ph\(_2\)CO as in Ph\(_2\)C(OH)C(SBu-t)=NH. Finally, the product can be easily rationalized by attack of H\(_2\)O upon Ph\(_2\)C=C(SBu-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 (CDCl₃) δ 7.30-7.16(m, lOH), 1.59(s, 9H); the MS was identical to that observed for 4c.

3-Phenylindole (6a)

Material synthesized according to the literature but using ZnCl₂ as the catalyst, had mp 85-86 °C(lit. 86-87 °C); ¹H NMR (CDCl₃) δ 8.24(br s, 1H, NH), 8.10-7.10(m, 1OH); ¹³C NMR (CDCl₃) 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 (CCl₄) at 3412 cm⁻¹; GC and HRMS, m/z (relative intensity) 194(15), 193.08917(M⁺, 100, calcd for C₁₄H₁₁N 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 (CDCl₃) δ 8.16(br s, 1H), 7.80-7.0(m, 14H); ¹³C NMR (CDCl₃) 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, calcld for C\textsubscript{20}H\textsubscript{15}NS, 301.0925), 267(10), 233(26), 165(7), 151(4), 134(5), 77(5).

**2-(
\textit{tert}-Butylthiyl\textit{)-3}-phenylindole (6c)**

Reaction of 1c (0.56 mmol) in 1 mL of (EtO)\textsubscript{3}P at 150 °C for 30 min gave a 95% isolated yield of the indole after flash column purification; mp 137-139 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \( \delta \) 8.16(br s, < 1H), 7.82-7.10(m, 9H), 1.13(s, 9H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \( \delta \) 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 (CCl\textsubscript{4}) at 3412 cm\textsuperscript{-1}; GC and HRMS, m/z (relative intensity) 283(0.7), 281.1233(M+, 11, calcld for C\textsubscript{18}H\textsubscript{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 absorption. However, absorption develops with time at 1620 cm\textsuperscript{-1} suggesting the formation of the 3H-indole.

**2-(Ethylthiyl)-3-phenylindole form the reaction of 1c with (EtO)\textsubscript{2}P(O)H**

Material isolated by column chromatography had mp 133-135 °C; FTIR (CCl\textsubscript{4}) at 3406, 1603 cm\textsuperscript{-1}; \textsuperscript{1}H 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 (calcd for C_{16}H_{15}NS 253.09253).

**S-tert-Butyl diphenylthioacetate**

Material isolated by column chromatography from the reactions of 1c with (EtO)_{2}P(O)H at 150 °C had \(^{1}H\) NMR (CDCl\(_{3}\)) \(\delta\) 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\(_{2}\)CHC(OEt)=NH)**

Material isolated by column chromatography from the reaction of 1c with (EtO)\(_{2}\)P(O)H at 150 °C had \(^{1}H\) NMR (CDCl\(_{3}\)) \(\delta\) 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)\(_{2}\)P(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 (CCl₄) at 3237 cm⁻¹; ¹H NMR (CDCl₃) δ 9.29(1H), 7.70-7.20(9H); ¹³C NMR (CDCl₃) 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 C₁₄H₁₀N₂O₂ 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 Ph₂S₂ by a literature procedure²⁷ has ¹H NMR (CDCl₃) 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 C₁₀H₁₅O₃PS 256.0480). The S-tert-butyl ester was identified by GCMS only; m/z (relative intensity) 226(M⁺, 1), 170(100), 142(30), 126(48), 114(43), 92(23), 57(60).

**α-(Diethoxyphosphinylnitrophenyl)phenylacetonitrile**

Reaction of 5 mmol of PhCH=CHNO₂ 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]=CH₂ (23%) and PhCH[P(O)(OEt)₂]=CH₂NO₂ (9%). The cyanophosphonate had FTIR (neat) at 2247 cm⁻¹; ¹H NMR (CDCl₃) 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 C₁₂H₁₆NO₃P 253.08679),
225(4), 197(3), 137(16), 117(90), 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=CHNO₂ 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=N=NOEt. A 15% yield of PhC[P(O)(OEt)₂]=CH₂P(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 (CDCl₃) 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 C₁₄H₂₀NO₄P 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 (CDCl₃) 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 C₁₆H₂₆NO₅P 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 (CDCl₃) 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 C₁₃H₂₀NO₄P 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 (Cl, 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 (CDCl₃) δ 7.86-6.94(m, 14H), 7.72(br s, 1H); ¹³C NMR (CDCl₃) 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 C₂₀H₁₅NO 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 $^1H$ NMR (CDCl$_3$) $\delta$ 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)$_3$P at 150 °C for 1 h followed by vacuum distillation of the volatiles gave 100% of 6e by $^1H$ 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); $^1H$ NMR (CDCl$_3$) $\delta$ 7.72 (br s, 1H, NH), 7.67-7.07 (m, 9H), 2.40 (s, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 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$_2$SO 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 $^1H$ 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 (CDCl₃) 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); ¹³C NMR (CDCl₃) δ 141.5(d, JPC=2.2 Hz), 140.7(d, JPC= 2.2 Hz), 128.2, 128.0, 127.9, 127.8, 127.1, 126.9, 62.0(d, JPOC=7.5 Hz), 61.9(d, JPOC=6.5 Hz), 54.1(d, JPC= 2.1 Hz), 40.6(d, ¹JPC=181 Hz), 17.2, 16.2,(d, JPC=6.0 Hz), 16.0(d, JPC=6.0 Hz); GC and HRMS, m/z, (relative intensity) 345(M⁺, 0.9), 344.14107(M⁻, 2.2, calcd for C₁₉H₂₃NO₃P 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 (8h) 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 CH₂Cl₂. The extract was washed, dried, filtered and concentrated to give by NMR (toluene was used as internal standard) 8h (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\(_3\)) \(\delta\) 10.05(br, s), 8.05-7.15(m, 9H), 4.04-3.78(m, 4H), 1.11(t, \(J=7.2\) Hz, 6H); \(^1^3\)C NMR (CDCl\(_3\)) \(\delta\) 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\(^+1^8\), 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\(_3\)) \(\delta\) 11.26(br, s), 7.82-7.05(m, 9H), 3.72-3.51(m, 4H), 0.929(t, \(J=6.9\) Hz, 6H); \(^1^3\)C NMR (CDCl\(_3\)) \(\delta\) 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\(^+1^8\), 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)$_3$P for 3 h gave by NMR with toluene as an internal standard, a 77% yield of 2 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 (Cl, 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 (Cl, 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$_3$P 331.13373), 240.0784(C$_{11}$H$_{15}$NO$_3$P+, 20), 194.0970(C$_{14}$H$_{12}$N+, 100). 193.0889(C$_{14}$H$_{11}$N+, 16), 104.0502(C$_{7}$H$_{6}$N+, 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$^{-1}$; $^1$H 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$^{-1}$; $^1$H 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-Phenyldinole (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); $^1$H NMR (CDCl$_3$) δ 8.34(br, s), 7.67-6.83(m, lOH).

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

cis-α-Nitrostilbene (1 mmol) in 15 mL of Me$_2$SO was added dropwise to a mixture of (EtO)$_2$P(O)H (10 mmol) and t-BuOK (5 mmol) in 25 mL of Me$_2$SO and the resulting solution stirred for 1 h before hydrolysis with brine. The product was extracted with CH$_2$Cl$_2$, washed and dried over Na$_2$SO$_4$, and concentrated to an oily residue. The NMR with toluene as an internal standard showed that it contained diethyl(2-nitro-1,2-diphenylethyl)phosphonate (28%). Flash column chromatography using hexane (75%) - ethyl acetate (25%) gave the phosphonate as a solid, mp 173-174 °C (from hexane dichloromethane); $^1$H 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$_3$P 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 Me₂SO 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%), PhCH₂C(Ph)=NOBu-t (6%) and [PhCHC(Ph)N(O)(OBu-t)]₂ (44%) (13% and 52% with Dabco or 6% of PhCH₂C(Ph)=NOBu-t and 48% of isobidesyl with PTSA), Ph₂C(OBu-t)CH=NOH from Ph₂C=CHNO₂ (up to 40% in the presence of PTSA), 3-phenyl-2-(phenylthiyl)indole (68% from Ph₂C=C(SPh)NO₂), 2-(*tert*-butylthiyl)-3-phenylindole (53% from Ph₂C=C(SBu-t)NO₂), and a mixture of 2-methyl-3-phenylindole (20%), Ph₂C=C(CH₃)N(Bu-t)OBu-t (12%) and [Ph₂C(OBu-t)C(CH₃)=N]₂O (28%) from Ph₂C=C(CH₃)NO₂. With 1.5 equiv. of *t*-BuHgCl/2KI, 2,2-diphenyl-3-(phenylthiyl)-2H-azirine is initially formed from Ph₂C=C(SPh)NO₂ in 60% conversion (40% yield). Nitroso aromatics react with *t*-BuHgX upon photolysis in Me₂SO 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*-Bu₆H₄)OBu-t (21%). Reactions of 2- or 4-substituted nitrobenzenes occur to generate *p*-HOC₆H₄N(Bu-t)OBu-t (28%), *p*-NCC₆H₄N(Bu-t)OBu-t (36%), *p*-OCHC₆H₄N(O)=NC₆H₄CHO-*p* (50%), *p*
PhCOC₆H₄N(O)=NC₆H₄COPh-p (47%), p-NCC₆H₄N(Bu-t)NH₄₆H₄CN-p (38%), p-Me₂N₆H₄N(Bu-t)OBu-t (34%) and p-Me₂N₆H₄N(Bu-t)H (21%). p-Dinitrobenzene yields p-t-Bu-C₆H₄NO₂ (25%) and p-t-Bu-C₆H₄N(Bu-t)OBu-t (20%) while the para halobenzenes yield p-BrC₆H₄N(Bu-t)OBu-t (15%) and p-BrC₆H₄N(Bu-t)H (25%), p-I₆H₄N(Bu-t)OBu-t (16%) and p-I₆H₄N(Bu-t)OH (28%). o-Nitrodiphenylaniline yields a mixture of o-C₆H₄NHC₆H₄NHBu-t (29%) and o-C₆H₄NHC₆H₄(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

\[
\begin{align*}
\text{PhNO}_2 + \text{PhMgX} &\rightarrow \text{PhNO}_2^+ \text{PhMgX}^- \\
2\text{PhMgX} &\rightarrow \text{PhNO}_2^+ \text{PhMgX}^- + \text{Ph-Ph} + \text{MgX}_2 + \text{MgO}
\end{align*}
\]
In 1976 Bartoli 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

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{ZJL} \\
\text{R} & \quad \text{11} \\
\text{ZJ} & \quad \text{L}
\end{align*}
\]

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

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

\[
\begin{align*}
\text{NO}_2 + 2\text{R}^1\text{MgX} &\rightarrow 2.4 \\
2.3 &\rightarrow 2.5 \\
\text{HCl} &\rightarrow 2.6 \\
\text{HCl} &\rightarrow 2.7 \\
\end{align*}
\]

\[ R = \text{n-C}_4\text{H}_9 \]

\[
\begin{align*}
\text{MeO} \text{N}_{\text{OMgX}} &\rightarrow 3.0 \\
\text{HCl} &\rightarrow 3.1 \\
\text{HCl} &\rightarrow 3.2
\end{align*}
\]
In 1990 Bartoli\(^7\) observed that allyl Grignard reagents reacted with nitroalkenes to generate addition products (Scheme V).

7-Substitution indoles can be synthesized from vinyl Grignard reagents by reaction with 2-substituted nitroarenes (Scheme VI).\(^8\)
In 1984 Corey synthesized di-tert-alkylamines according to Scheme VII.9

The conversion of the tert-alkylamines to the tert-alkynitroso compounds was accomplished by using peracetic acid in ethyl acetate. The tert-alkynitroso compound was then reacted with tert-butyl radicals formed from the oxidation of tert-butylhydrazine with PbO2. 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 organometallic compounds. Russell\textsuperscript{10} observed an ESR signal in the reaction of nitrobenzene with \textit{n}-butyllithium in THF/hexane (3:1). Hoffmann\textsuperscript{11} reported that free radicals were identified in the reaction of nitro compounds with organoalkali compounds and Maruyama\textsuperscript{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 \textit{t}-BuHgX/KI with 1-nitroalkenes and aromatic nitroso or nitro compounds.
RESULTS AND DISCUSSION

The combination of $t$-BuHgI and KI in Me$_2$SO will reduce enoyl radicals to enolate anions\textsuperscript{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 $\beta$-nitrostyrenes yield a series of interesting compounds depending upon the nature of the $\alpha$ or $\beta$ substituents. Reaction of $\beta$-nitrostyrene with $t$-BuHgX/KI generates in 40\% yield the substitution product PhCH=CHBu-$t$ (44) expected from $\beta$-addition of $t$-Bu$^-$ followed by loss of NO$_2$.\textsuperscript{14,16} (E)-PhCH=C(Ph)NO$_2$ reacted with $t$-BuHgI/KI to generate 6\% of PhCH$_2$C(Ph)=NOBu-$t$ (45) and 44\% of the dimer [PhCHC(Ph)N(O)(OBu-$t$)]$_2$ (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$_2$SO the products were 6\% of 45, a small amount of 46 and 48\% of isobidesyl,\textsuperscript{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 IX

\[
\text{R} = \text{t-Bu}
\]

\[
\text{PhCH}=\text{C(Ph)}\text{NO}_2 \xrightarrow{\text{hv}} \text{PhCH}=\text{C(Ph)}\text{NO}_2^* \\
\text{PhCH}=\text{C(Ph)}\text{NO}_2^* \xrightarrow{\text{RHgI}_2^-} \text{PhCH}=\text{C(Ph)}\text{NO}_2^- + \text{R}^- + \text{HgI}_2 \\
\]

\[
\text{PhCH}=\text{C(Ph)}\text{NO}_2^- \xrightarrow{\text{RHgX or PhCH}=\text{C(Ph)}\text{NO}_2} \text{PhCH}=\text{C(Ph)}\text{NO}_2^- + \text{R}^- \\
\text{PhCH}=\text{C(Ph)}\text{NO}_2^- \xrightarrow{\text{H}_2\text{O}^+} \text{PhCH}=\text{C(Ph)}\text{-Ph} \xrightarrow{\text{isobidesyl}} \text{PhCH}=\text{C(Ph)}\text{-Ph}
\]
1-Nitro-1-X-2,2-diphenylethynes fail to form dimers analogous to 46, presumably because of steric reasons. Instead, they are deoxygenated to yield 2H-azirines and/or indoles as shown in Scheme X.

Scheme X

A minor product Ph₂CHC(O)NH(OBu-t) (47) observed from Ph₂C=C(SR)NO₂ is consistent with the formation of Ph₂C=C(SR)N(HgCl)OBu-t and its hydrolysis to 47 via Ph₂C=C(SR)NHOBu-t. Table 1 list the different conditions employed and the products observed for the reaction of Ph₂C=C(SR)NO₂ with t-BuHgX/KI.
Table 1. Photostimulated reactions of $t$-BuHgX with Ph$_2$C=C(SR)NO$_2$ in Me$_2$SO$^a$

\[
\text{Ph}_2\text{C}=\text{C(SR)NO}_2 + t\text{-BuHgX} + \text{KI} \rightarrow \text{Ph}_2\text{C} \equiv \text{C} \overset{\text{N-SR}}{\text{C}} + \text{Ph}_2\text{CHC(O)NH(OBu-)}_\text{Bu-t} + \text{I}_2 \text{-SR}
\]

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time</th>
<th>% Yield$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp X t-BuHgX: KI: (h)</td>
<td>1b 4b 6b 47 6c 1c</td>
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<tr>
<td>1b R=Ph - - : 4 : 25 + - - - -</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>1c R=Bu-t - - : 8c : 25 + - - - -</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b Cl 2 : 5 : 13 tr - 68 10 - -</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b Cl 1.5 : 3 : 17 30 40f - tr - -</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b Cl 1.5 : 3 : 18d tr total 52 tr - -</td>
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<td></td>
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<tr>
<td>1c - - : 10 : 24 - - - - - +</td>
<td></td>
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<tr>
<td>1c I 2 : - : 28e - - - - - +</td>
<td></td>
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<tr>
<td>1c Cl 3 : 6 : 24 - - - 2 10 53</td>
<td></td>
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</tr>
<tr>
<td>1c I 3 : 6 : 8 - - - 9 53 -</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1. (Continued)

a 0.1-0.2 M of Ph$_2$C=C(SR)NO$_2$ in 10 mL of Me$_2$SO illuminated with a 275-W General Electric sunlamp at about 40 °C.

b By GC and $^1$H 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$_2$C=C(SPh)NH(0Bu-t) or Ph$_2$C=C(SPh)N(OH)Bu-t or Ph$_2$C(0Bu-t)C(SPh)=NOH.

1-Nitro-2,2-diphenylethylene (1a) and 1-methyl-1-nitro-2,2-diphenylethylene (1e) also underwent deoxygenation by $t$-BuHgl/KI to generate indoles and alkoxy oximes (Tables 2 and 3). With 1a in the presence of PTSA the product Ph$_2$C(0Bu-t)CH=NOH (48) was formed in 40% yield and the substitution product Ph$_2$C=CHBu-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 $t$-BuHgl/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 \( t\text{-BuHgX} \) with \( \text{Ph}_2\text{C}=\text{CHNO}_2 \) in \( \text{Me}_2\text{SO} \)

\[
\text{Ph}_2\text{C}=\text{CHNO}_2 + t\text{-BuHgX} + \text{KI} + [ ] \xrightarrow{\text{hv}} \text{la}
\]

\[
\begin{array}{cccccc}
\text{Comp} & X & t\text{-BuHgX:} & \text{KI:} & \text{P or D} & \text{Time} & \% \text{Yield} \\
\text{la} & I & 2: & - & 26 & + & - & - \\
\text{la} & Cl & 2: 4: & - & 8 & 90 & tr & tr & tr \\
\text{la} & I & 2: 2.5: & - & 27 & 19 & 8 & 5 & 5 \\
\text{la} & I & 3.5: 3.5: 3.5(P) & 43 & - & 40 & 10 & tr \\
\text{la} & I & 3: 3: 3(D) & 26 & tr & 8 & 14 & tr \\
\end{array}
\]

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

---

\( a \) 0.1-0.2 M of \( \text{la} \) in 10 mL of \( \text{Me}_2\text{SO} \) irradiated with a 275-W General Electric sunlamp at about 40 °C.

\( b \) By GC and \( ^1\text{H} \) NMR with toluene as an internal standard.

\( c \) \( \text{(P)} \) means PTSA and \( \text{(D)} \) means Dabco, which are the chemical reagents for "[ ]" in the reaction.
Table 3. Photostimulated reactions of t-BuHgX with Ph₂C=C(CH₃)NO₂ in Me₂SO

\[
\text{Ph}_2\text{C}=\text{C}(\text{CH}_3)\text{NO}_2 + \text{t-BuHgX} + \text{KI} + [ ] \xrightarrow{\text{hv}}
\]

\[
\text{1e}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{H} & \quad \text{CH}_3 \\
\end{align*}
\]

\[
\text{6e}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{OBU-t} & \quad \text{CH}_3 \\
\end{align*}
\]

\[
\text{5.2}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{OCH}_2\text{SCH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

\[
\text{5.3}
\]

\[
\text{5.1}
\]

\[
\text{5.0}
\]

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time</th>
<th>% Yieldb</th>
</tr>
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<tbody>
<tr>
<td>Comp X t-BuHgX: KI: P or Dc</td>
<td>(h)</td>
<td>5.0</td>
</tr>
<tr>
<td>1e I 4 : 8 : 4(P)</td>
<td>23 tr</td>
<td>tr</td>
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<tr>
<td>1e I 4 : 8 : -</td>
<td>23 10 20</td>
<td>tr</td>
</tr>
<tr>
<td>1e I 4 : 8 : 4(D)</td>
<td>17 12 28 20 tr</td>
<td>tr</td>
</tr>
</tbody>
</table>

a 0.1-0.2 M of 1e in 10 mL of Me₂SO 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.
The intermediate nitroso compounds derived from the \( \beta \)-nitrostyrenes appear to react preferentially with \( t-Bu \cdot \) 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 Me₂SO 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

\[
\begin{align*}
\text{Ph-N}=0 & \quad \xrightarrow{\text{hv}} \quad (\text{Ph-N}=0^*)_{n-n^*} \quad \text{triplet} \\
\text{Ph-N}=0^* + \text{t-BuHgCl} & \quad \xrightarrow{\text{Bu-}} \quad \text{Ph-N-O}^* \quad \text{Bu-t} \quad \xrightarrow{\text{HgCl}} \quad \text{Ph-N-OBu-t} \\
\text{Ph-N}=0^* & \quad \xrightarrow{\text{Bu-}} \quad \text{Ph-N-O}^* \quad \text{HgCl} \quad \xrightarrow{\text{Bu-}} \quad \text{Ph-N-OBu-t} \\
\text{Ph-N-HgCl} & \quad \xrightarrow{\text{Bu-}} \quad \text{Ph-N-OBu-t} \quad \xrightarrow{\text{HgCl}} \quad \text{Ph-N(O)=N-Ph}
\end{align*}
\]
Table 4. Photostimulated reactions of \( t\)-BuHgX with nitrosobenzene and \( o\)-nitrosotoluene in Me\(_2\)SO\(^a\)

\[
\begin{align*}
\text{Molar equivalents} & & \text{Time (h)} & & \% \text{Yield}^b \\
R & X & t\text{-BuHgX} & & 58 & 60 \\
\text{H} & \text{Cl} & 2 & 24 & 98 & - \\
\text{H} & \text{Cl} & 5 & 24 \text{ (dark)} & 33 & - \\
\text{H} & \text{Cl} & 2 & 44 & 100^c & - \\
\text{H} & \text{I} & 2 & 25 & 90^d & - \\
\text{H} & \text{I} & 2 & 24 & 63^e & - \\
\text{H} & \text{I} & 5 & 24 \text{ (dark)}^f & 51 & - \\
\text{CH}_3 & \text{Cl} & 2 & 23 & - & 50^g \\
\text{CH}_3 & \text{Cl} & 2 & 44 & - & 67^h \\
\text{CH}_3 & \text{I} & 2 & 36 & - & 50 \\
\end{align*}
\]

\(^a\) 0.1-0.2 M of nitrosobenzene or \( o\)-nitrosotoluene in 10 mL of Me\(_2\)SO irradiated with a 275-W General Electric sunlamp at about 40 °C.
Table 4. (Continued)

b By GC or \(^1\)H NMR with toluene as an internal standard.
c Cis/trans ratio = 4:1 by GC.
d Me\(_2\)SO 10 mL with 1 mL of TFA, Z:E = 27:1 in GC.
e Me\(_2\)SO 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 \((\text{EtO})_3\text{P}\) 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 \((\text{61})\).

The presence of CH\(_3\)CO\(_2\)H or CF\(_3\)CO\(_2\)H did not prevent the formation of the azoxy compounds from PhNO or o-MeC\(_6\)H\(_4\)NO. In the presence of acids presumably PhN(HgX)OBu-\(t\) is converted to PhNHOBu-\(t\) which undergoes condensation with unreacted PhNO.
RHgI$_2^-$ is a 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 $N$-$\text{tert}$-butyl-$N$-arylhydroxylamines and the $N$-$\text{tert}$-butyl-$N$-$\text{tert}$-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-\(t\)-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 Hgl\(_2\) or Hgl to the nitroxide which could be reduced back to 63 by \(t\)-BuHgl\(_2\) 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 \(t\)-\(t\)-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\(_6\)H\(_4\)N(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 Hgl\(_2\) and RC\(_6\)H\(_4\)N(R)OR with Hgl\(_2\).
Scheme XIII

R=t-Bu

\[
\begin{align*}
\text{Ph-NO}_2 & \xrightarrow{\text{hv}} \text{Ph-NO}_2^* \xrightarrow{\text{RHgI}_2^-} \text{PhNO}_2^- + R^- + \text{HgI}_2 \rightarrow \text{PhN(OR)O}^- \\
& \rightarrow \text{PhNO} + \text{RO}^- \\
\text{PhNO} & \rightarrow \text{PhNO}^* + \text{RHgI}_2^- \rightarrow \text{PhNO}^- + R^- + \text{HgI}_2 \\
\text{PhNO}^- + \text{RHgI}^- & \rightarrow \text{PhNO} + R^- + \text{Hg}^0 + I^- \\
\text{PhNO}^- + R^- & \rightarrow \text{PhN(R)O}^- \\
\text{PhNO} + R^- & \rightarrow \text{PhN(R)O}^- \xrightarrow{R^-} \text{PhN(R)OR} \\
\text{PhN(R)O}^- + \text{RHgI}_2^- & \rightarrow \text{PhN(R)O}^- \\
\text{PhNO}^- + \text{H}^+ & \rightarrow \text{Ph-NOH} \xleftarrow{\text{PhNHO}^- + R^-} [\text{PhNHOR}] \\
\text{PhNHOR} + \text{PhNO} & \rightarrow \text{PhN(O)=NPh} + \text{HOR}
\end{align*}
\]
Table 5. Photostimulated reactions of \( t\)-BuHgX with nitrosobenzene and nitrobenzene in Me\(_2\)SO\(^a\)

\[
\begin{array}{ccc}
\text{NO} & \text{NO}_2 & \text{R}=\text{t-Bu} \\
\text{5.7} & \text{2.3} & \text{+ t-BuHgX + KI + [ ]} \\
\text{RC}_6\text{H}_4\text{N(R)}\text{OR} & \text{9.5} \\
\text{5.8} & \text{6.5} & \\
\end{array}
\]

![Chemical structures](image)

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<tr>
<th>Molar equivalents</th>
<th>Time</th>
<th>% Yield</th>
<th>Comp</th>
<th>t-BuHgX(^c):</th>
<th>KI: P or D(^d)</th>
<th>(h)</th>
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<tr>
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<td>15</td>
<td>17</td>
<td>8</td>
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Table 5. (continued)

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<tr>
<th>Comp</th>
<th>t-BuHgX</th>
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<th>Time</th>
<th>% Yield</th>
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<td>65</td>
<td>10</td>
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<td>12</td>
<td>21</td>
<td>38</td>
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<td>5:5:2</td>
<td>36</td>
<td>62</td>
<td>23</td>
</tr>
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<td>2.3</td>
<td>2:5:2</td>
<td>48</td>
<td>37</td>
<td>6</td>
</tr>
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</tr>
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<td>48</td>
<td>8</td>
<td>4</td>
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<tr>
<td>2.3</td>
<td>2:5:3</td>
<td>31</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>2.3</td>
<td>2:5:5</td>
<td>25</td>
<td>58</td>
<td>39</td>
</tr>
<tr>
<td>2.3</td>
<td>5:5:1</td>
<td>24</td>
<td>35</td>
<td>tr</td>
</tr>
</tbody>
</table>

- a 0.1-0.2 M of 57, 63, or 23 in 1-10 mL of Me2SO 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 (CH3)3COK.
- g Dark reaction with 32% of nitrosobenzene recovered.
- h 5 Equiv. of K2S2O8.
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 Me₂SO. t-BuHgX in Me₂SO 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

\[
\text{PhCHO} \xrightarrow{\text{deoxygenation}} \text{PhCH=NHPh}
\]

\(66\)

\(o\)-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 \( \alpha \)-elimination to form \( \text{ArN} \); which was rapidly trapped by \( t\)-BuHgX to form \( \text{ArN(HgX)Bu-t} \) which yielded the aniline upon hydrolytic workup. Compound 73b is believed to be formed by the deoxygenation of compound 73a\textsuperscript{18} followed by photolysis.

\[
\begin{align*}
\text{NO} & \quad \text{CH}_3 \\
+ t\text{-BuHgX} + \text{KI} + \text{Y} & \quad \rightarrow \\
\text{R} & \quad \text{N} \quad \text{OR} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{59} & \\
\text{R}=t\text{-Bu} & \\
\text{67} & \\
\text{68} &
\end{align*}
\]

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

\[
\begin{align*}
\text{60} & \\
13\% & \\
4\% &
\end{align*}
\]

\[
\begin{align*}
\text{69b} & \\
\text{tr} & \\
- &
\end{align*}
\]

* 1:2:5 Represents the ratio of the equivalents of the reactants and 39 h means reaction time.
\[
\text{X} = \text{Cl} \quad \text{(1:2:5 and 25 h)} \\
\text{X} = \text{I} \quad \text{Y} = \text{Dabco} \quad \text{(1:4:10:3 and 12 h)} \\
\text{X} = \text{I} \quad \text{Y} = \text{PTSA} \quad \text{(1:4:10:3 and 6 h)}
\]
Mono-, di- and trisubstituted nitrobenzene derivatives have been used as substrates to react with Grignard reagents.\textsuperscript{5,7,8} Photochemical reaction of 2- or 4-substituted nitrobenzenes with $t$-BuHgX/KI in Me\textsubscript{2}SO can yield a variety of products as shown in the reactions, which are listed in the following pages (pp. 90-93).

The mechanism of these reactions XC\textsubscript{6}H\textsubscript{4}NO\textsubscript{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\textsubscript{2}SO yielded N-\textit{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-\textit{tert}-butylated derivative assigned structure 109a.

![Chemical structures](#)
\[
\text{NO}_2^+ + \text{t-BuHgX} + \text{KI} + \text{Y} \rightarrow \text{NNPh} + \text{NNPh}
\]

7.5

X = Cl \hspace{1cm} (1:4:10 and 23 h) \hspace{1cm} 17% \hspace{1cm} 29%

X = I \hspace{1cm} Y = \text{Dabco} \hspace{1cm} (1:4:10:4 and 23 h) \hspace{1cm} 28% \hspace{1cm} 13%

7.6

7.7

7.8

7.9

R = t-Bu

8.0 \hspace{1cm} (1:2:2:1 and 38 h)

8.1 \hspace{1cm} (28%)

8.2 \hspace{1cm} (1:2:5 and 48 h)

8.3 \hspace{1cm} (56%)

8.4 \hspace{1cm} (4%)
NO₂

+ t-BuHgI + KI → NC−N−N−CN

R H

8.5 (1:4:10 and 24 h) 8.6 (38%)

RO

R

N

N

+ NC

+ NC

8.7 (36%) 8.8 (15%) R=t-Bu

NO₂

COPh

+ t-BuHgX + KI + Y → PhOC−N=N−COPh

O

8.9

X=Cl Y=Dabco (1:5:10:5 and 39 h) 9.0

X=I (1:4:5 and 48 h) 14%

R=Cl

R=I

RO

R

N

N

+ COPh

+ COPh

9.1

10%

23%

9.2

10%

20%
R = t-Bu

\[
\text{NO}_2
\]

\[
\text{R} = \text{f-BuHgCl} + \text{KI} \rightarrow \text{R} \quad + \quad \text{RC}_6\text{H}_4\text{N(R)OR}
\]

93 (1:4:10 and 36 h)

94 (25%)

95 (20%)

\[
\text{OCH}_2\text{SCH}_3
\]

\[
\text{R} \quad + \quad \text{NH}
\]

96 (19%)

97 (5%)

\[
\text{NO}_2
\]

\[
\text{I}
\]

\[
\text{X=C1 Y=Dabco (1:5:10:5 and 38 h) 8% 19%}
\]

\[
\text{X=I (1:3:6 and 23 h) 6% 12%}
\]

\[
\text{X=I Y=Dabco (1:5:5:5 and 30 h) 16% 28%}
\]

\[
\text{X=I Y=PTSA (1:5:5:5 and 30 h) 20% 13%}
\]

101

\[
\text{N}
\]

102

\[
\text{H}
\]

\[
\text{I}
\]

\[
\text{R} \quad + \quad \text{RC}_6\text{H}_4\text{NO}_2 \quad + \quad \text{tr}
\]

101

\[
\text{N}
\]

102

\[
\text{H}
\]

\[
\text{I}
\]

\[
\text{R} \quad + \quad \text{J}
\]

7% 6%

\[
\text{tr}
\]

\[
\text{tr}
\]
$\text{BrNO}_2 + t\text{-BuHgX} + \text{KI} + Y \rightarrow \text{RO}_2N + \text{R}_2N\text{OH}$

103

<table>
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<th>Reaction</th>
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<tr>
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<td>6%</td>
<td>18%</td>
</tr>
<tr>
<td>$X=\text{I}$ (1:3:6 and 23 h)</td>
<td>8%</td>
<td>-</td>
</tr>
<tr>
<td>$X=\text{I}$ Y=Dabco (1:5:5:5 and 30 h)</td>
<td>15%</td>
<td>25%</td>
</tr>
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</table>

$\text{H}_2\text{N}_2\text{Br} + \text{RC}_6\text{H}_4\text{NO}_2$

106

<table>
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<th>Reaction</th>
<th>Products</th>
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<td>-</td>
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<tr>
<td>14%</td>
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<tr>
<td>-</td>
<td>7%</td>
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</table>
Scheme XV

\[
\begin{align*}
\text{NO}_2 & \rightarrow \text{NO} \\
\text{R} & \rightarrow \text{NOR} \\
\text{Hg} & \rightarrow \text{NOR} \\
\text{ArNO} & \rightarrow \text{N-OH} \\
\text{N-} & \rightarrow \text{HgX} \\
\text{OH} & \rightarrow \text{N-} \\
\text{R} & \rightarrow \text{R-} \\
\text{N-} & \rightarrow \text{N-} \\
\text{Hg} & \rightarrow \text{N-} \\
\text{X} & \rightarrow \text{X} \\
\end{align*}
\]

\text{R} = \text{t-Bu}

\text{excess ArNO} \rightarrow \text{azoxy compounds}

\text{Dabco}

\text{N-OH} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow \text{N-} \rightarrow

Scheme XVI

\[
\begin{align*}
\text{Scheme XVI} & \\
\text{95} & \\
\end{align*}
\]
An isomer of \textbf{109a}, compound \textbf{109c} was formed in 24\% yield from the photolysis of 2-hydroxyquinoline with $t$-BuHgCl/KI/Dabco (1:4:10:5). Compound \textbf{109a} and \textbf{109c} were not interconverted by treatment with PTSA in Me$_2$SO and cannot be simple enol-keto tautomers.

Structure \textbf{109a} is a rather surprising product from a reaction of quinoline N-oxide. However, the following spectroscopic data seems to demand either structure \textbf{109a} or \textbf{109b}.

(a) a normal aromatic ring in $^1$H ($\delta^H=7.2-7.4$) and $^{13}$C NMR
(b) two tert-butyl groups, one attached to a saturated carbon ($\delta^H=0.9$) and one attached to a vinyl carbon or a heteroatom ($\delta^H=1.3$)
(c) two methine carbons (doublets in $^{13}$C NMR) at $\delta$ 61.3 and 54.5
(d) a saturated methine carbon containing a heteroatom substituent at $\delta^H=4.7$
(e) a hydroxy group at 3281 cm$^{-1}$
(f) probably a C=N group at 1614 cm$^{-1}$
(g) the partial structure based on $^1$H NMR coupling constants, in the presence of D$_2$O the $\delta=1.6$ hydrogen and the coupling with $J=9.6$ Hz disappear

\[
\begin{array}{c}
\xymatrix{
C \ar[r] & H \\
& C \ar[r] & H \\
& & O \\
& & \delta^H 2.6 \\
& & 4.7 \\
& & 1.6
}
\end{array}
\]

(h) CI and EI MS consistent with the formula weight of 259, HRMS and
elemental analysis consistent with the composition C₁₇H₂₅NO.

If the quinoline ring is retained, only structures 109a and 109b are possible. Structure 109b should readily lose H₂O to form 2,4-di-tert-butylquinoline. 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 H₂O 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
CONCLUSION

Nitroarenes, nitrosoarenes or the β-nitrostyrenes PhC(Z)=C(Y)NO₂ 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, CH₃), 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 PhNO₂ 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-Packard 3390A integrator. ¹H NMR spectra were recorded on a 300-MHz Nicolet NT 300 spectrometer with tetramethylsilane as the integral standard. GC/MS were recorded on a Finnegan 4000 spectrometer and HRMS were recorded on an AEI MS 902 mass spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point 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 calcium hydride. Other solvents were purchased and used without purification. Me₂SO-d₆ was purchased from Cambridge Isotope Laboratories and dried over 4A molecular sieves. (E)-PhCH=C(Ph)NO₂ 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 MgSO₄, evaporation and recrystallization to give the needle of t-BuHgCl: mp 110-113 °C; ¹H NMR (CDCl₃) δ 1.51(s, 9H).
**tert-Butylmercury iodide**

$t$-BuHgCl was mixed with a two-fold excess of KI in Me$_2$SO and stirred 2 hours and worked up as described for the preparation of $t$-BuHgCl. The $t$-BuHgl had $^1$H NMR (CDCl$_3$) $\delta$ 1.43 (s, 9H).

**3,3-Dimethyl-1-phenylbutene (44)$^{14,16}$**

$\beta$-Nitrostyrene (2.0 mmol), $t$-BuHgCl (4.0 mmol) and KI (10.0 mmol) were dissolved in 10 mL of Me$_2$SO 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 chloride. 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$_2$SO$_4$, and concentrated under vacuum. The mixture was analyzed by $^1$H 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 $^1$H 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$_2$SO was added under nitrogen. With stirring the
solution was irradiated 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 chloride. The organic extract was washed with saturated sodium thiosulfate, dried over anhydrous Na₂SO₄, 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 (CDCl₃) δ 7.41-7.06(m,10H), 3.86(s, 2H), 1.31(s, 9H); ¹³C NMR (CDCl₃) 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 C₁₈H₂₁NO 267.16236), 211(53), 193(66), 178(4), 165(5), 120(5), 103(4), 91(65), 77(12), 57(100).

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

Compound 46 was isolated as solid with mp 185-186 °C; ¹H NMR (CDCl₃) δ 7.51-7.04(m, 16H), 6.23(d, J=6.9Hz, 4H), 5.20(br, 2H), 1.01(br, 18H); ¹³C NMR (CDCl₃) 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\textsubscript{36}H\textsubscript{40}N\textsubscript{2}O\textsubscript{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)**

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

**3-Phenylthiyl-2,2-diphenyl-2-\(\text{H}\)-azirine (4b)**

Compound 4b was isolated as a solid with FTIR at 1600 cm\(^{-1}\); 1H NMR (CDCl\(_3\)) \(\delta\) 7.32-6.99(m); 13C NMR (CDCl\(_3\)) \(\delta\) 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\textsubscript{20}H\textsubscript{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-\text{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\(_3\)) \(\delta\) 7.34-7.24(m, 10H),
5.416(br, <1H), 4.81(s, 1H), 1.32(s, 9H); 13C NMR (CDCl3) 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 C18H21NO2 283.15655), 183(19), 167(100), 152(0.3), 91(1.0), 77(1.3), 57(49).
Anal. Calcd for C18H21NO2; 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 (CDCl3) 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 C18H22NO2 284.16506), 266.15397(C18H20NO+), 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+NH4+, 0.4), 284(M+1+, 86), 266(11), 217(7), 200(100), 183(30), 167(1). Anal. Calcd for C18H21NO2: 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 (CDCl3) δ 7.62-7.04(m, 10H), 1.83(s, 3H), 1.05(s, 9H); 13C NMR(CDCl3) 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 C23H31NO 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 (CDCl₃) δ 7.45-7.11 (m, 20H), 1.508 (s, 6H), 1.192 (s, 18H); ¹³C NMR (CDCl₃) 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(C₂₅H₂₇NO⁺, 1.1), 296.16510(C₁₉H₂₂NO₂⁺, 5.6), 280.16989(C₁₉H₂₂NO⁺, 21.2), 224.10709(C₁₅H₁₄NO⁺, 100), 105.03431(C₇H₅O⁺, 14). All fragments were within 2.0 ppm of the assigned atomic composition. GCMS (CI, methane), m/z (relative intensity) 617(M+C₃H₅⁺, 0.2), 605(M+C₂H₅⁺, 0.4), 577(M+H⁺, 8), 521(0.4), 394(0.9), 280(100), 224(66), 183(53), 167(11), 105(12).


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 Me₂SO. 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 chromatography 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$_3$) $\delta$ 7.64-7.05(m, 9H), 2.47(s, 3H), 1.51(s, 9H); $^{13}$C NMR (CDCl$_3$) $\delta$ 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-(Methylsulfinylmethoxy)-2-methyl-3-phenylindole (53)**

A trace of compound 53 was isolated as a liquid; $^1$H NMR (CDCl$_3$) $\delta$ 7.66-7.09(m, 9H), 5.30(s, 2H), 2.55(s, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 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$_3$) $\delta$ 7.26-7.16(m, 3H), 7.08-7.01(m, 2H), 1.07(s, 9H), 1.05(s, 9H); $^{13}$C NMR (CDCl$_3$) $\delta$ 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 (CDCl₃) 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 (d₆-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); ¹³C NMR (CDCl₃) 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-\textit{tert}-Butoxy-\textit{tert}-butyl-\textit{o}-toluidine (67)

Compound 67 was isolated as a liquid; $^1$H NMR (CDCl$_3$) $^\delta$ 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-\textit{tert}-Butyl-\textit{o}-toluidine (68)

Compound 68 was isolated as a liquid contaminated with a trace of compound 60; $^1$H NMR (CDCl$_3$) $^\delta$ 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-\textit{tert}-Butyl-\textit{N}-hydroxytoluidine (69a)$^{19}$

N-\textit{tert}-Butyl-\textit{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-\textit{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 $^\delta$ 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$_3$) $\delta$ 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$_2$O), 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$_3$) $\delta$ 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$_3$) $\delta$ 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 isolated and had an $^1$H NMR identical with the material purchased from Aldrich Chemical Company.
p-Dimethylamino-N-tert-butynitroxide (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 (CDCl3) 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 C₂₀H₂₈N₂O 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 (CDCl₃) 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 C₁₆H₂₀N₂ 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$_2$O$_3$ 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+,
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 (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₈H₁₈N₄ 290.15315), 234(100), 207(2), 143(5), 117(8), 102(21), 57(60).

p-CN-tert-Butoxy-N-tert-butylamino'benzonitrile (87)

Compound 87 was isolated as a liquid with FTIR at 2226 cm⁻¹; ¹H NMR (CDCl₃) 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 C₁₅H₂₅N₂O 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 (CDCl₃) 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 C₁₁H₁₄N₂O 190.11062), 174(19), 159(50), 143(11), 134(92),
4,4'-Azoxydibenzophenone (90)

Compound 21 was isolated as a solid, mp 198.5-199.5 °C; $^1$H NMR (CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$O$_3$ 406.13174), 390(6), 197(10), 181(46), 153(15), 105(100), 77(30).

p-(N-tert-Butoxy-N-tert-butylamino)benzophenone (91)

Compound 21 was isolated had $^1$H NMR (CDCl$_3$) $\delta$ 7.81-7.31(m, 9H), 1.13(s, 9H), 1.08(s, 9H); $^{13}$C NMR (CDCl$_3$) $\delta$ 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$^+$, 2, calcd for C$_{21}$H$_{28}$NO$_2$ 326.21200), 325.20524(C$_{21}$H$_{27}$NO$_2$$^+$, 0.5), 269(15), 252(3), 238(2), 213(100), 182(1), 136(13), 105(24), 77(15), 57(64); GCMS (Cl, ammonia), m/z (relative intensity) 343(M$+$NH$_4^+$, 19), 326(M$+$H$^+$, 100), 254(22).

p-(N-tert-Butylamino)benzophenone (92)

Compound 22 was as solid, mp 126-130 °C; FTIR at 3427, 1655 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 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; $^1$H NMR (CDCl$_3$) $\delta$ 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; $^1$H NMR (CDCl$_3$) $\delta$ 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$_8$H$_9$NO$_3$S 199.03032), 76(3), 61(100).

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

Compound 97 was isolated as a liquid; $^1$H NMR (CDCl$_3$) $\delta$ 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$_2$O$_2$ 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 $^\circ$C; $^1$H NMR (CDCl$_3$) $\delta$ 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\textsubscript{14}H\textsubscript{22}INO 347.07462), 291(16), 235((17), 218(5), 127(0.1), 108(4), 91(2), 77(2), 76(7), 57(100).

\textbf{N-\textit{tert}-Butyl-p-iodophenylhydroxylamine (100)\textsuperscript{20}}

Compound \textbf{100} was isolated as a solid, mp 119-120 °C with FTIR at 3381 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) $\delta$ 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\textsubscript{10}H\textsubscript{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\textsubscript{4}+, 27), 292(M+H\textsuperscript{+}), 276(100), 166(14), 150(14).

\textbf{p-Iodo-N-\textit{tert}-butylaniline (101)\textsuperscript{20}}

Compound \textbf{101} was isolated as a liquid with FTIR at 3410 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) $\delta$ 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\textsubscript{10}H\textsubscript{14}IN 275.01710), 260(94), 244(3), 219(100), 148(4), 77(5), 57(49).

\textbf{p-Bromo-N-\textit{tert}-butoxy-N-\textit{tert}-butylaniline (104)\textsuperscript{20}}

Compound \textbf{104} was isolated as a solid, mp 38-39 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) $\delta$ 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\textsubscript{14}H\textsubscript{22}BrNO 299.08848), 245(8), 243(10), 228(3), 226(2),
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189(41), 187(39), 108(2), 91(2), 77(1), 57(100).

*p-Bromo-N-tert-butylphenylhydroxylamine (105)*

Compound 105 was isolated as a solid, mp 130-132 °C with FTIR at 3209 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 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)*

Compound 106 was isolated as a liquid with FTIR at 3406 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 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\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 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 (CDCl₃) 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 (CDCl₃ plus D₂O) δ 4.51 (s), 2.67 (s), 1.65 (no absorption); ¹³C NMR (CDCl₃) 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 C₁₇H₂₅NO 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⁺, 100), 186 (3), Anal. Calcd. for C₁₇H₂₅NO: 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 (CDCl₃) 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 C₁₇H₂₅NO 259.19361), 201 (29), 186 (32), 167 (14), 159 (65), 146 (100), 117 (8), 57 (13).
REFERENCES


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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Ames, IA 50011
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 \( \text{111} \). This reaction leads to adduct radical \( \text{112} \) that must be converted to non-radical products before polymerization occurs. Polymerization is avoided either by intermolecular trapping of the adduct radical \( \text{112} \) or by intramolecular homolytic bond cleavage. Hydrogen atom donors \( X-H \) or heteroatom donors \( X-Z \) are used as trapping agents.

\[
\begin{align*}
\text{R}^- + \text{C} = \text{C}^\cdot \rightarrow \text{R}^-\text{C} = \text{C}^\cdot \\
\text{110} & \quad \text{111} & \quad \text{112} \\
& & \text{113} \\
& & \text{114}
\end{align*}
\]

In this competition system, alkyl radical \( \text{110} \) must react faster with the alkene than with \( HX \) or \( XZ \) and adduct the radical \( \text{112} \) 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 \( \text{110} \) one has to use alkenes \( \text{111} \) with electron-withdrawing groups \( Y \) that reduce the
nucleophilic character of the adduct radicals. 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 NaBH₄ or Bu₃SnH leads to alkylmercury hydrides that trap alkyl radicals to form product. Reactive alkenes like acrylonitrile, vinyl ketones, arylates, fumarodinitrile, or maleic anhydrides react with alkyl radicals in the presence of NaBH₄ to form high yields of products.

Russell et.al. has reported that chain reactions between alkylmercury halides and some deficient alkenes [CH₂=CH(EWG)] involving Eq. 1, e.g. with EWG = PhSO₂ or (EtO)₂P(O).³

\[
R^- + CH₂=CH(EWG) \xrightarrow{NaBH₄} RCH₂CH(EWG) \xrightarrow{HgCl} RCH₂CH₂(EWG) + Hg^0
\] (1)
Although α,β-unsaturated carbonyl compounds react inefficiently with RHgCl when photostimulated, reactions occur readily in the presence of iodide ion in Me₂SO by virtue of electron transfer between the adduct enolyl radical and RHgI₂⁻, Eq. 2.4,5 However, adduct radicals from α,β-unsaturated nitriles do not undergo this reaction efficiently.

\[
RCH₂ĊHC(O)Y + RHgI₂⁻ \rightarrow RCH₂CH=C(O)Y + R \cdot + HgI₂
\]  
(2)

We have found that intermediate adduct radicals such as,

\[
\text{RCH}(R')\hat{C}(Y)≡N \quad \text{or} \quad \text{RCH}(R')\hat{C}(Y)≡NR²
\]

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

\[
\hat{\zeta}=\hat{C}=\text{NH}^+ + \text{RHgI}_2 \xrightarrow{\text{Me}_2\text{SO}} \hat{\zeta}=\hat{C}=\text{NH} + R \cdot + \text{HgI}_2
\]  
(3)

\[
\hat{\zeta}=\text{C}(Y)\text{NH}(R')^+ + \text{RHgI}_2 \xrightarrow{\text{Me}_2\text{SO}} \hat{\zeta}=\text{C}(Y)\text{NH}(R') + R \cdot + \text{HgI}_2
\]  
(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-
BuCH₂CH₂CONH₂. In Me₂SO(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

\[
\begin{align*}
\text{OM} & \quad \text{R'} \\
\text{N} & \quad \text{C} \\
\text{R} & \quad \text{R} \\
\end{align*}
\]

(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.)

\[
\begin{align*}
\text{CH}(\text{R}')\text{CH}(\text{R}'')\text{CMe}_3 & \quad \text{PTSA} \\
\end{align*}
\]
RESULTS AND DISCUSSION

Reactions of tert-butyl radicals with acrylonitrile

Acrylonitrile reacted slowly upon photolysis in the presence of t-BuHgl/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 Me2SO(1)-EtOH(1) the ketenimine can be trapped by

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

\[
\text{RCH}_2\text{CH}=\text{C}=\text{NH} + \text{EtOH} \rightarrow \text{RCH}_2\text{CH}_2\text{C}=\text{NH} \rightarrow \text{RCH}_2\text{CH}_2\text{C}^+ \text{OEt} \rightarrow \text{RCH}_2\text{CH}_2\text{C}^+ \text{OEt}
\]

Table 1. Alkylation of acrylonitrile by t-BuHgI in Me\textsubscript{2}SO\textsuperscript{a}

\[
\text{H}_2\text{C}=\text{CHCN} + \text{t-BuHgI} + [ ] \stackrel{\text{hv}}{\rightarrow} \text{Me}_3\text{CCH}_2\text{CH}_2\text{CN} + \text{Me}_3\text{CH}_2\text{CH}_2\text{CONH}_2
\]

\[
+ \text{Me}_3\text{CCH}_2\text{CH}_2\text{COOEt}
\]

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time (h)</th>
<th>% Yield\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-BuHgI: KI: D or P</td>
<td>Time (h)</td>
<td>116</td>
</tr>
<tr>
<td>3 : 3 : 0</td>
<td>23</td>
<td>tr</td>
</tr>
<tr>
<td>2 : 4 : 2 (D)</td>
<td>48</td>
<td>30</td>
</tr>
<tr>
<td>3 : 3 : 3 (P)</td>
<td>23</td>
<td>33</td>
</tr>
<tr>
<td>5 : 5 : 5 (P)</td>
<td>23</td>
<td>40</td>
</tr>
<tr>
<td>2 : 2 : 0</td>
<td>48</td>
<td>33\textsuperscript{d}</td>
</tr>
<tr>
<td>5 : 5 : 5 (P)</td>
<td>24</td>
<td>13\textsuperscript{e}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 0.05-0.2 M of acrylonitrile in 10 mL of Me\textsubscript{2}SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

\textsuperscript{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 \textsuperscript{120} and amide \textsuperscript{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 NaBH\textsubscript{4} to form the saturated adduct in a low yield from 33-37\%.

\[
\begin{align*}
\ce{c-C6H11- + C==C-C-CN &<\rightarrow C6H_{11}C==C-C-CN | 33\%} \\
\ce{c-C6H11- + C==C-C-CN &<\rightarrow C6H_{11}C==C-C-CN | 37\%}
\end{align*}
\]
Table 2. Photostimulated reactions of $t$-BuHgl with crotononitrile
$(E, Z$-mixture) in Me$_2$SO$^a$

$$\text{MeCH}=\text{CHCN} + t\text{-BuHgl} + \left[ \right] \xrightarrow{\text{hv}} \text{Me}_3\text{CCHMeCH}_2\text{CN} + \text{Me}_3\text{CCHMeCH}_2\text{CONH}_2$$

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time (h)</th>
<th>% Yield$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-BuHgl: KI: PTSA$^c$</td>
<td>120</td>
<td>121</td>
</tr>
<tr>
<td>2: 2: 0</td>
<td>23</td>
<td>16</td>
</tr>
<tr>
<td>2: 2: 3</td>
<td>23</td>
<td>60</td>
</tr>
</tbody>
</table>

$^a$ 0.05-0.2 M of crotononitrile in 10 mL of Me$_2$SO 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$_4$. 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 \( \alpha\)-chloroacrylonitrile in Me\( _2\)SO\(^a\)

\[
\text{H}_2\text{C}=\text{C}(\text{CN})\text{Cl} + t\text{-BuHgI} + \left[ \right] \xrightarrow{\text{hv}} \text{Me}_3\text{CCH}(_2\text{CH}((\text{CN})\text{Cl} + [\text{Me}_3\text{CCH}_2(\text{CN})\text{Cl}]_2
\]

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time (h)</th>
<th>% Yield(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t)-BuHgI: KI: (D) or (P)(^c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5:5:0</td>
<td>23</td>
<td>20</td>
</tr>
<tr>
<td>2:4:2(D)</td>
<td>47</td>
<td>12</td>
</tr>
<tr>
<td>5:5:5(P)</td>
<td>36</td>
<td>65</td>
</tr>
</tbody>
</table>

\(^a\) 0.05-0.2 M of \( \alpha\)-chloroacrylonitrile in 10 mL of Me\( _2\)SO 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-\( \alpha\)-cyanocinnamate, \( \alpha\)-phenylcinnamonomitrile 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.

Electron withdrawing substituents on the alkene, which lower the LUMO energy, increase the rate of addition by reducing the SOMO-LUMO energy gap. Some representative relative reactivity data determined by Giese in competitive reactions with \( \text{c-C}6\text{H}_11\text{HgCl/NaBH}_4 \) are given below.

<table>
<thead>
<tr>
<th></th>
<th>( \text{C}_4\text{H}_9 )</th>
<th>( \text{C}_6\text{H}_5 )</th>
<th>( \text{CO}_2\text{CH}_3 )</th>
<th>( \text{CHO} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific</td>
<td>1.0</td>
<td>84</td>
<td>3000</td>
<td>8500</td>
</tr>
</tbody>
</table>

Comparing methacrylonitrile to \( \alpha \)-phenylcinnammonitrile and ethyl trans-\( \alpha \)-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-BuHgI2- 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-BuHgCl and Dabco to methacrylonitrile increase from 2 to 5 equivalents. Possibly the Dabco can form a complex with t-BuHgCl which is a better reducing agent than t-BuHgI2- or maybe the Dabco is a hydrogen atom donor to the electrophilic adduct radical.

\[ R\cdot + \overset{c}{\underset{d}{\text{C}}}_d \rightarrow R\overset{c}{\underset{d}{\text{C}}}_d \rightarrow \left( \overset{c}{\underset{d}{\text{R}}}_d \right)_2 \]

\( c: \) capto (electron-withdrawing) substituent
\( d: \) dative (electron-releasing) substituent
Reaction of α-phenylcinnamonicnitrile 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

\[ R - C - C = C = \text{CN} \]

135
Table 4. Photostimulated reactions of \( t\)-BuHgI with ethyl \((E)\)-\( \alpha \)-cyanocinnamate in Me\(_2\)SO\(^a\)

\[
\text{PhCH=CC(N)COOEt} + t\text{-BuHgI} + [ ] \xrightarrow{hv} \text{Me}_3\text{CCHPhCN(COOEt)H}
\]

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time (h)</th>
<th>% Yield(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t)-BuHgI: KI: (D) or (P)(^c)</td>
<td>22</td>
<td>77(^d)</td>
</tr>
<tr>
<td>2 : 4 : 2 (D)</td>
<td>22</td>
<td>83</td>
</tr>
<tr>
<td>4 : 4 : 4 (P)</td>
<td>22</td>
<td>83</td>
</tr>
</tbody>
</table>

\(^a\) 0.05-0.2 M of ethyl \((E)\)-\( \alpha \)-cyanocinnamate in 10 mL of Me\(_2\)SO 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$_2$SO$^a$

\[
\text{H}_2\text{C}=\text{CMeCN}+t\text{-BuHgI} + [ \xrightarrow{\text{hu}} \text{Me}_3\text{CCH}_2\text{CH(Me)CN} + [\text{Me}_3\text{CCH}_2\text{C(Me)CN}]_2 ]
\]

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time (h)</th>
<th>% Yield$^b$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>t-BuHgI: KI: (D) or (P)$^c$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 : 4 : 0</td>
<td>47</td>
<td>30</td>
<td>46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 : 5 : 5 (D)</td>
<td>20</td>
<td>60</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 : 3 : 3 (P)</td>
<td>23</td>
<td>tr</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 : 5 : 3 (P)</td>
<td>19</td>
<td>tr</td>
<td>60$^d$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 0.1-0.2 M of methacrylonitrile in 10 mL of Me$_2$SO 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 $t$-BuHgl with $\alpha$-phenyl-cinnamoniitrile in Me$_2$SO$^a$

\[
\begin{align*}
\text{PhCH}=\text{CPhCN} + t\text{-BuHgl} + [ ] & \xrightarrow{\text{hv}} \text{Me}_3\text{CCHPhCHPhCN} \\
\text{13.0} & \\
+ \text{Me}_3\text{CCHPhCH(p-C}_6\text{H}_4\text{CMe}_3)\text{CN} + \text{Me}_3\text{CCHPhCHPhCONHMe}_3 \\
\text{13.2} & \text{13.3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time (h)</th>
<th>$%$ Yield$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$-BuHgl: KI: (D) or (P)$^c$</td>
<td>13.1</td>
<td>13.2</td>
</tr>
<tr>
<td>2 : 4 : 0</td>
<td>96</td>
<td>46$^d$</td>
</tr>
<tr>
<td>2 : 4 : 2 (D)</td>
<td>96</td>
<td>31$^d$</td>
</tr>
<tr>
<td>5 : 5 : 5 (P)</td>
<td>36</td>
<td>$\sim$50</td>
</tr>
</tbody>
</table>

$^a$ 0.1 M of $\alpha$-phenylcinnamoniitrile in 10 mL of Me$_2$SO 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 $\alpha$-phenylcinnamoniitrile remained at the end of the reaction.

$^f$ Mixture of diastereomers.
Reactions of *tert*-butyl radical with alkylidemalononitriles and benzylidemalononitrile

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.\textsuperscript{8} In the case of β-Me group, the rate retarding effect (or reversibility of a radical addition to an olefin) can be counterbalanced by placing two cyano groups in a geminal position of the alkene.\textsuperscript{10} This concept has been utilized for the preparation of alkanoic acids by coupling alkylidemalononitriles with alkyl radicals generated from the alkylmercuric chlorides and NaBH\textsubscript{4}, followed by hydrolysis and decarboxylation. The required cyano olefins have been prepared by the Knoevenagel reaction of aldehyde or ketones with malononitrile.

\[
\begin{align*}
R^1\text{CHO} + CH_2(CN)CN & \rightarrow R^1\text{CH—C(CN)CN} \\
R^1R^2\text{CH—CH(CN)CN} & \rightarrow R^1R^2\text{CHCH}_2\text{COOH}
\end{align*}
\]

Similar results have been observed in reactions α,β-unsaturated dinitriles such as benzylidemalononitrile or isopropylidemalononitrile 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

\[ R^1R^2C=\text{C(CN)}_2 + R \cdot \xrightarrow{\text{RHgX}_2^-} R^2C\text{C(CN)}_2 + \text{H}^+ \]
Table 7. Photostimulated reactions of \( t\)-BuHgI with benzyldiene-
malononitrile in \( \text{Me}_2\text{SO} \)^a

\[
\text{PhCH}=\text{C(CN)}_2 + t\text{-BuHgI} + [\text{hv}] \rightarrow \text{Me}_3\text{CCH(Ph)CH(CN)}_2 + \text{Me}_3\text{CC(Ph)=C(CN)}_2
\]

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time (h)</th>
<th>% Yield^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t)-BuHgI: KI: (D) or (P)^c</td>
<td>( \text{Me}_3\text{CCH(Ph)CH(CN)}_2 )</td>
<td>( \text{Me}_3\text{CC(Ph)=C(CN)}_2 )</td>
</tr>
<tr>
<td>2 : 4 : 0</td>
<td>17</td>
<td>41</td>
</tr>
<tr>
<td>2 : 4 : 2 (D)</td>
<td>47</td>
<td>70</td>
</tr>
<tr>
<td>2 : 4 : 4 (P)</td>
<td>23</td>
<td>91</td>
</tr>
<tr>
<td>4 : 4 : 4 (P)</td>
<td>22</td>
<td>99</td>
</tr>
</tbody>
</table>

^a 0.05-0.2 M of \( \text{PhCH}=\text{C(CN)}_2 \) in 10 mL of \( \text{Me}_2\text{SO} \) 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$_2$HgCl with benzylidene-
malononitrile in Me$_2$SO$^a$

\[
\text{PhCH} = \text{C(CN)$_2$} + \text{PhCH$_2$HgCl} + \left[ \right] \xrightarrow{\text{hv}} \text{PhCH$_2$CH(Ph)CH(CN)$_2$} + \text{PhCH$_2$CH(CN)$_2$}
\]

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time (h)</th>
<th>% Yield$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$-BuHgl: KI: Dabco$^c$</td>
<td>1.34</td>
<td>1.37</td>
</tr>
<tr>
<td>2 : 0 : 2</td>
<td>72</td>
<td>50</td>
</tr>
<tr>
<td>2 : 4 : 2</td>
<td>33</td>
<td>~50</td>
</tr>
</tbody>
</table>

$^a$ 0.2 M of PhCH=C(CN)$_2$ in 10 mL of Me$_2$SO 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$_2$SO

\[ \text{(R}^1\text{)}(\text{R}^2)=\text{C(CN)}_2 + \text{t-BuHgI} + [ ] \xrightarrow{\text{hv}} \text{Me}_3\text{CC(R}^1\text{)}(\text{R}^2)\text{CH(CN)}_2 \]

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time (h)</th>
<th>% Yield$^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-BuHgI: KI: PTSA$^c$</td>
<td></td>
<td>140</td>
</tr>
<tr>
<td>3 : 0 : 0</td>
<td>23</td>
<td>37$^d$</td>
</tr>
<tr>
<td>3 : 3 : 0</td>
<td>23</td>
<td>68</td>
</tr>
<tr>
<td>3 : 3 : 3</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>4 : 8 : 0</td>
<td>18</td>
<td>-</td>
</tr>
<tr>
<td>2 : 2 : 3</td>
<td>26</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ 0.05-0.2 M of cyclohexylidenemalononitrile or isopropylidenemalononitrile in 10 mL of Me$_2$SO 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 TCNO (7,7,8,8-tetracyanoquinodimethane) with tert-butyl radical

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

\[
\begin{align*}
\text{NC} & \quad \text{C} & \quad \text{CN} \\
\text{NC} & \quad \text{C} & \quad \text{CN} \\
\end{align*}
\]

Photolysis of TCNO 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.

\[
\begin{align*}
\text{NC} & \quad \text{C} & \quad \text{CN} \\
\end{align*}
\]

In the presence of Dabco the product is a black tar and a trace of $\alpha,\alpha'$-di-$t$-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 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 ketones also have been reported.

The reaction was proposed to proceed via 1,4-addition to form the ketenimine intermediate which can be hydrolyzed to the aldehyde. Introduction of a base followed by hydrolysis yields the ketone.
Addition 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$_2$SO$^a$

\[
\begin{align*}
\text{148} & \quad + t\text{-BuHgI} + [ ] \quad \xrightarrow{hv} \\
\text{149} & \quad \quad \quad \quad 150
\end{align*}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>t-BuHgI:</th>
<th>KI:</th>
<th>D or P$^c$</th>
<th>Time (h)</th>
<th>% Yield$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>148</td>
<td>2 : 4 : 0</td>
<td></td>
<td></td>
<td>48</td>
<td>~57 ~18</td>
</tr>
<tr>
<td>148</td>
<td>2 : 4 : 2 (D)</td>
<td></td>
<td></td>
<td>48</td>
<td>~33 ~33</td>
</tr>
<tr>
<td>148</td>
<td>2 : 4 : 0</td>
<td></td>
<td></td>
<td>38</td>
<td>66$^d$ trace</td>
</tr>
<tr>
<td>148</td>
<td>5 : 5 : 3 (P)</td>
<td></td>
<td></td>
<td>23</td>
<td>95</td>
</tr>
</tbody>
</table>

$^a$ 0.05-0.2 M of oxazines in 10 mL of Me$_2$SO 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$_2$SO 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$_2$SO$^a$

\[
\begin{align*}
\text{Ph} & \quad \text{O} & \quad \text{N} & \quad \text{N} & \quad \text{O} & \quad \text{Ph} \\
\end{align*}
\]

\[
\begin{align*}
+ & \quad t\text{-BuHgI} + [ ] & \quad \text{hv} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{O} & \quad \text{N} & \quad \text{N} & \quad \text{O} & \quad \text{Ph} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{O} & \quad \text{N} & \quad \text{N} & \quad \text{O} & \quad \text{Ph} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$t$-BuHgI:</th>
<th>KI:</th>
<th>D or Pc</th>
<th>Time (h)</th>
<th>% Yield$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>151</td>
<td>5 : 5 : 0</td>
<td></td>
<td></td>
<td>20</td>
<td>trace ~40</td>
</tr>
<tr>
<td>151</td>
<td>5 : 5 : 5 (D)</td>
<td></td>
<td></td>
<td>20</td>
<td>trace ~40</td>
</tr>
<tr>
<td>151</td>
<td>5 : 5 : 5 (D)</td>
<td></td>
<td></td>
<td>24</td>
<td>trace &gt;82</td>
</tr>
<tr>
<td>151</td>
<td>5 : 5 : 0</td>
<td></td>
<td></td>
<td>20</td>
<td>~13 ~24$^d$</td>
</tr>
<tr>
<td>151</td>
<td>5 : 5 : 5 (P)</td>
<td></td>
<td></td>
<td>20</td>
<td>&gt;95 trace</td>
</tr>
</tbody>
</table>

$^a$ 0.05-0.2 M of oxazines in 10 mL of Me$_2$SO 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$_2$SO 8 mL.
Table 12. Photostimulated reactions of t-BuHgI with 2-(β-styryl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine in Me₂SO

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>t-BuHgI: KI: PTSA</th>
<th>Time (h)</th>
<th>% Yield^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>154</td>
<td>5 : 5 : 0</td>
<td>20</td>
<td>no reaction</td>
</tr>
<tr>
<td>154</td>
<td>5 : 5 : 0</td>
<td>20</td>
<td>63^d ~30</td>
</tr>
<tr>
<td>154</td>
<td>5 : 5 : 5</td>
<td>20</td>
<td>6.5 ~15</td>
</tr>
</tbody>
</table>

a 0.05-0.2 M of oxazines in 10 mL of Me₂SO 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 Me₂SO 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 $\alpha,\beta$-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

\[
\text{NC} = \text{CN} + i-\text{Pr} \rightarrow \text{NC} = \text{CH} = \text{CN} \rightarrow \text{NC} \quad \text{H}^+ \rightarrow \text{C} = \text{CH} = \text{C} = \text{NH}^+ \\
\text{Dabco} \rightarrow \text{NC} \quad \text{H} \rightarrow \text{RHgI}_2^-
\]

\[
i-\text{PrCH(CN)CH} = \text{C} = \text{NH} \rightarrow \text{i-PrCH(CN)CH}_2\text{CN}
\]

\[
\text{C} = \text{C} \quad \text{CH}_2\text{CN} \rightarrow \text{C} = \text{C} \quad \text{CH}_2\text{CN} + \text{R} \cdot + \text{Hg}^\circ + \text{X}^-
\]

\[
i-\text{Pr} \rightarrow \text{NC} \quad \text{H} \rightarrow \text{CN}
\]

\[
(1) \cdot \text{H}^+ \quad (2) \cdot \text{e}^-
\]

\[
\text{NC} = \text{C} = \text{CN}
\]
Table 13. Photostimulated reactions of \( i\text{-PrHgCl} \) with fumaronitrile and its derivatives in \( \text{Me}_2\text{SO}^a \)

\[
\begin{align*}
\text{NC} & \quad \text{C} = \quad \text{H} \\
\text{H} & \quad \text{C} = \quad \text{NC} \\
\text{NC} & \quad \text{C} = \quad \text{CN} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} - \text{CH}_2\text{CN} & \quad + \quad \text{C} = \quad \text{C} = \quad \text{CN} & \quad + \quad \text{C} - \quad \text{C} - \quad \text{C} = \quad \text{N} - <
\end{align*}
\]

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time</th>
<th>% Yield</th>
<th>( 159 )</th>
<th>( 160 )</th>
<th>( 158 )</th>
<th>( 161 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>( i\text{-PrHgCl} ): KI: D or P (^c)</td>
<td>( (h) )</td>
<td>( 159 )</td>
<td>( 160 )</td>
<td>( 158 )</td>
<td>( 161 )</td>
</tr>
<tr>
<td>( 157 )</td>
<td>2 : 4 : 3 (P)</td>
<td>22</td>
<td>87</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( 157 )</td>
<td>1 : 2 : 1 (D)</td>
<td>2</td>
<td>-</td>
<td>55</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>( 157 )</td>
<td>2 : 4 : 2 (D)</td>
<td>2</td>
<td>-</td>
<td>40</td>
<td>48</td>
<td>tr</td>
</tr>
<tr>
<td>( 157 )</td>
<td>4 : 0 : 4 (D)</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( 158 )</td>
<td>5 : 10 : 5 (D)</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>67</td>
<td>33</td>
</tr>
<tr>
<td>( 158 )</td>
<td>5 : 10 : 3 (P)</td>
<td>17</td>
<td>-</td>
<td>-</td>
<td>44</td>
<td>48</td>
</tr>
<tr>
<td>( 158 )</td>
<td>10 : 20 : 3 (P)</td>
<td>48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>tr</td>
</tr>
</tbody>
</table>

\( ^a \) 0.02-0.2 M of \( 157 \) or \( 158 \) in 10 mL of \( \text{Me}_2\text{SO} \) 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 Me₂SO

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Comp.</strong></td>
<td><strong>t-BuHgCl: KI: D or Pc</strong></td>
<td>(h)</td>
</tr>
<tr>
<td><strong>1567</strong></td>
<td>2:2:2 (P)</td>
<td>23</td>
</tr>
<tr>
<td><strong>1567</strong></td>
<td>2:0:0</td>
<td>23</td>
</tr>
<tr>
<td><strong>1567</strong></td>
<td>2:2:0</td>
<td>23</td>
</tr>
<tr>
<td><strong>1567</strong></td>
<td>2:0:4 (D)</td>
<td>2</td>
</tr>
<tr>
<td><strong>1567</strong></td>
<td>1:1:1 (D)</td>
<td>2</td>
</tr>
<tr>
<td><strong>1567</strong></td>
<td>2:2:2 (D)</td>
<td>3</td>
</tr>
</tbody>
</table>
Table 14. (continued)

<table>
<thead>
<tr>
<th>Molar equivalents</th>
<th>Time</th>
<th>% Yield&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comp.</td>
<td>t-BuHgCl: KI: D or P&lt;sup&gt;c&lt;/sup&gt;</td>
<td>(h)</td>
</tr>
<tr>
<td>157</td>
<td>2 : 2 : 2 (D)</td>
<td>15</td>
</tr>
<tr>
<td>157</td>
<td>4 : 4 : 4 (D)</td>
<td>2</td>
</tr>
<tr>
<td>157</td>
<td>4 : 4 : 4 (D)</td>
<td>6</td>
</tr>
<tr>
<td>162</td>
<td>5 : 5 : 5 (D)</td>
<td>2</td>
</tr>
<tr>
<td>162</td>
<td>5 : 5 : 3 (P)</td>
<td>24</td>
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<tr>
<td>163</td>
<td>5 : 5 : 3 (P)</td>
<td>24</td>
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<sup>a</sup> 0.01-0.2 M of 157, 162 or 163 in 10 mL of Me<sub>2</sub>SO irradiated with a 275-W General Electric sunlamp at about 40 °C.

<sup>b</sup> By NMR with toluene as an internal standard.

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

<sup>d</sup> A small amount of Me<sub>3</sub>CH(CN)COCMe<sub>3</sub> (167) also was isolated presumably from hydrolysis of 163.
The photostimulated reductive alkylation of $\alpha,\beta$-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$_3$C$_6$H$_4$SO$_3$H. 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 $^1$H 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, $\alpha$-chloroacrylonitrile, $\alpha$-phenylcinnammonitrile, 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-(\(\alpha\)-Styryl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine was prepared by modifying the literature procedures.$^7$

2-(\(\beta\)-Styryl)-4,4,6-trimethyl-5,6-dihydro-1,3-oxazine was
prepared by modifying the literature procedure. 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 Me₂SO was added under nitrogen. 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 NaHCO₃ 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 Na₂SO₄, 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 (CDCl₃) 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. mp 140-141 °C); FTIR (CDCl₃) at 3352, 3188, 1666 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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$_7$H$_{15}$NO 129.11536), 114(31), 97(17), 73(65), 72(100), 57(39).

General procedure for photostimulated alkylations of acrylonitrile in Me$_2$SO-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$_2$SO 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 $^1$H 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; $^1$H NMR (CDCl$_3$) $\delta$ 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$_9$H$_{19}$O$_2$ 159.1385), 158.13253(M+, 0.3, calcd for C$_9$H$_{18}$O$_2$ 158.1307), 143.10728(M-15+, 21.2, calcd for C$_8$H$_{15}$O$_2$ 143.1072), 113.09712(M-45+, 33.2, calcd for C$_7$H$_{10}$O 113.0967), 102.06845(M-56+, 59.1, calcd for C$_5$H$_{10}$O$_2$ 102.0681), 97(52), 85(7), 74(26), 69(66), 57(100), 41(55); GCMS (Cl, ammonia), m/z (relative intensity) 334(2M+18+,
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$_2$SO was irradiated under nitrogen. After irradiation, the solution was worked up as described previously and analyzed by $^1$H 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 $^1$H NMR (CDCl$_3$) $\delta$ 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$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 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$_8$H$_{17}$NO 143.13101), 128(17), 124(5), 110(6), 87(61),
General procedure for photostimulated alkylations of $\alpha$-chloroacrylonitrile

A mixture of $\alpha$-chloroacrylonitrile (1 mmol), $t$-BuHgI (5 mmol), KI (5 mmol) and PTSA (5 mmol) in 10 mL of Me$_2$SO 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)

Compound 123 was isolated by flash column chromatography with hexane (95%) - ethyl acetate (5%); $^1$H NMR (CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_6$H$_9$CIN 130.04235), 94(34), 89(6), 67(24), 57(100). The $^1$H NMR was the same as the spectra data in literature.8

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

Compound 124 was isolated as solid, mp 103-104 °C (hexane); $^1$H NMR (CDCl$_3$) $\delta$ 2.533(s, 4H), 1.088(s, 18H); $^{13}$C NMR (CDCl$_3$) $\delta$ 129.0, 117.0, 47.5, 33.9, 29.4; GC and HRMS, m/z (relative intensity)
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 Me2SO 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 (CDCl3) 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 C16H21NO2 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 Me2SO and irradiated
under nitrogen. After worked up 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)butanenitrile (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 (CDCl₃) 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⁺, 5), 110(42), 83(10), 69(32), 57(100), 41(50).

2,3-Dimethyl-2,3-bis(2,2-dimethylpropyl)butanenitrile (129)

Compound 129 was formed as 1:1 mixture of diastereomers on judged from ¹H NMR analysis of the crude product. The diastereomers were separated by column chromatography. One diastereomer had mp 122-123 °C and ¹H NMR (CDCl₃) 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 C₁₆H₂₈N₂ 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 (CDCl₃) 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⁺,
Photostimulated reaction of α-phenylcinnamonicnitrile with t-BuHgl in the presence of Dabco

A mixture of α-phenylcinnamonicnitrile (1 mmol), t-BuHgl (5 mmol), KI (5 mmol) and PTSA (5 mmol) in 10 mL of Me2SO 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 (CDCl3) δ 7.25-6.94(m, 1OH), 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 C19H21N 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 (CDCl3) 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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 TCNO (7,7,8,8-tetracyanoquinodimethane)

The substrate (0.5-2.0 mmol), RHgX and coreactants were dissolved in 10 mL of deoxygenated Me2SO 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 Na2SO4, 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)

The compound had 1H NMR (CDCl3) 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); 13C NMR (CDCl3) 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 C14H16N2
α-Cyano-β-tert-butylcinnamonicitrile (136)\textsuperscript{16}

This compound was isolated as a solid, mp 108-112 °C (lit.\textsuperscript{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-Diphenylethymlmalononitrile (137)\textsuperscript{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)\textsuperscript{17,18}

The compound was isolated as a white solid, mp 81-83 °C (lit.\textsuperscript{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$_8$N$_2$ 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\(_3\)) \(\delta\) 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\(_{9}\)H\(_{13}\)N\(_{2}\) 149.10787), 122(1), 108(9), 99(2), 93(0.4), 83(23), 69(7), 57(100).

**α-tert-Butyl-α-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\(_3\)) \(\delta\) 7.68(qt, \(J=8.4, 2.1\) Hz, 4H), 5.21(br, 1H), 1.221(s, 9H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 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
General procedure for photostimulated alkylations of oxazines

The substrate (0.5-2 mmol), i-BuHgI and coreactants were dissolved in 10 mL of deoxygenated Me2SO 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 Na2SO4, 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)

Compound 149 was a colorless liquid which had 1H NMR (CDCl3) 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 C14H26NO 224.20144), 210.108605(M-15+, 47, calcd for C13H24NO 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$_3$) $\delta$ 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-1+, very small, calcd for C$_{28}$H$_{51}$N$_2$O$_2$ 447.39505), 433.37907(M-15+, 1.3, calcd for C$_{27}$H$_{49}$N$_2$O$_2$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$O$_2$ 572.43418), 515(100), 332(4), 250(7), 230(8), 205(5), 180(4), 131(14), 103(47), 83(31),
Compound 155 was a liquid; $^1$H NMR (CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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) 287.2246 (M+, 38, calcd for C$_{19}$H$_{29}$NO), 272 (71), 231 (35), 190 (3), 154 (6), 148 (8), 134 (10), 130 (22), 105 (29), 91 (36), 77 (9), 58 (100), 57 (30).

Compound 156 was a liquid; $^1$H NMR (CDCl$_3$) $\delta$ 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) 571.4260 (M-1+, 10, calcd for C$_{38}$H$_{55}$N$_2$O$_2$), 557.4107 (M-15+, 2, calcd for C$_{37}$H$_{53}$N$_2$O$_2$), 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 substrate (0.02-0.2 mmol), RHgX and coreactants were dissolved in 10 mL of deoxygenated Me$_2$SO 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 Na₂SO₄, 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)

Compound 159 had (lit.²⁰ decomposition 180-190 °C) ¹H NMR (CDCl₃) 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 C₇H₁₁N₂ 123.09222), 121.07625(M⁻1⁺, 1.2, calcd for C₇H₉N₂ 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 (CDCl₃) δ 3.31(s, 2H), 2.17(s, 3H), 1.98(s, 3H); ¹³C NMR (CDCl₃) 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 C7H8N2 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 (CDCl3) 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 C10H14N2 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 (CDCl3)
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); 13C NMR (CDCl3) 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 C16H28N2 248.22525), 233(2),
205(7), 163(100), 133(4), 121(18), 94(4), 67(4). Elemental analysis
calculated for C16H28N2 : C, 77.36; H, 11.36; N, 11.28. Found: C, 77.38;
H, 10.97; N, 11.45.

2-tert-Butylbutanenitrile (164)

Compound 164 was a solid, mp 89-89.5 °C (lit.8 bp 420 K/0.2
mmHg); 1H NMR (CDCl3) 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-\textit{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$_8$H$_{10}$N$_2$ 134.08440), 133.07671(M-1+, 8, calcd for C$_8$H$_9$N$_2$ 137.07657), 119(100), 107(26), 107(30), 92(65), 76(11), 65(37), 57(57).

2,3-Di-\textit{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-\textit{tert}-butylbutanenitrile (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 (Cl, 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$_3$) $\delta$ 2.57 (s, 2H), 1.16 (s, 18H); $^{13}$C NMR (CDCl$_3$) $\delta$ 118.3, 41.6, 34.3, 27.4; GC and HRMS, m/z (relative intensity) 193.17095 (M$^+$, 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$^+$, 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$O 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$_2$O: 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$_3$) $\delta$ 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$_3$) $\delta$ 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$^+$, 2, calcd for C$_{16}$H$_{31}$N$_2$O 267.24364), 251.21191 (M-15$^+$, 2, calcd for C$_{15}$H$_{27}$N$_2$O 251.21234), 226 (2), 209 (12), 195 (3), 184 (33), 166 (2), 153 (69), 128 (21), 110 (16),
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\(_3\)) \(\delta\) 3.740 (s, 1H), 1.22 (s, 9H), 1.16 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 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).
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\(_3\)) \(\delta\) 3.740(s, 1H), 1.22(s, 9H), 1.16(s, 9H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 206.0, 116.7, 46.4, 45.7, 35.2, 27.9, 26.1; GC and HRMS, m/z (relative intensity) 182.15461(M\(^+\), 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).
REFERENCES

GENERAL SUMMARY

The reactions of Ph₂C=C(Y)NO₂ (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 phosphite in Me₂SO at room temperature (Y=H, CH₃, SBU-t) or by triethyl phosphite at 150 °C (Y=H, CH₃, 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 nitroso compounds in a manner analogous to the reactions of Grignard reagents. Based on the reaction products observed it is concluded that the reactions of t-BuHgI/KI with nitro compounds follows the scheme, RNO₂ → RN(OBu-t)OHgI → RNO → RN(OBu-t)HgI → RN(Bu-t)HgI.

Promotion of electron transfer 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.
LITERATURE CITED


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