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THE REACTION OF CARBANIONS WITH tert-BUTYL RADICALS[1]

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Abstract—The $S_{RN}1$ free radical chain reaction of Me_3CHgCl with nitronate ($^-O_2N{=}C(R_1)(R_2)$) and phenone enolate ($PhC(O^-){=}C(R_1)(R_2)$) anions yields the C-alkylation products ($Me_3CC(R_1)(R_2)NO_2$, $PhCOC(R_1)(R_2)CMe_3$). Competitive reactions between pairs of anions demonstrate that as the basicity of the anion increases the reactivity toward $Me_3C\cdot$ at first increases and then decreases. An inverted reactivity order is also observed with phenylacetonitrile anions. In early transition state reactions, the nucleophilic character of the tert-butyl radical apparently controls the reactivity by virtue of a transition state involving transfer of the electron from radical to the LUMO of the resonance stabilized anion.

Alkylmercury halides will participate in a photostimulated free radical chain reaction with the anions of nitroalkanes according to Scheme 1.[2] Evidence for this $S_{RN}1$ mechanism

$$R\cdot + (R_1)(R_2)C{=}NO_2^- \longrightarrow R{-}C(R_1)(R_2){-}NO_2\cdot^- \qquad (1)$$

$$R{-}C(R_1)(R_2){-}NO_2\cdot^- + RHgX \longrightarrow R{-}C(R_1)(R_2){-}NO_2 + RHgX\cdot^- \qquad (2)$$

$$RHgX\cdot^- \longrightarrow R\cdot + Hg^\circ + X^- \qquad (3)$$

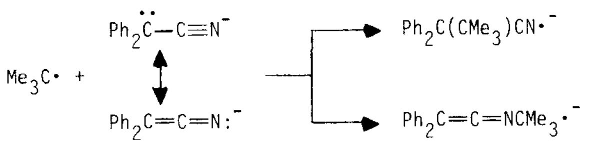
Scheme 1

includes the cyclization of $R\cdot$ = 1-hexenyl to the cyclopentylcarbinyl radical and its subsequent trapping by $Me_2C{=}NO_2^-$.[3] Scheme 1 shows $RHgX\cdot^-$ as an intermediate. Actually, the electron transfer to RHgX is believed to be dissociative with reactions 2 and 3 of Scheme 1 occurring in a concerted manner. The basis for tentatively excluding $RHgCl\cdot^-$ as an intermediate is that the reactivity of RHgCl in competitive reactions is determined by the stability of $R\cdot$. Thus, reactions of 5-10 equivalents of a 1:1 mixture of Me_3CHgCl and RHgCl with $Me_2C{=}NO_2^-$ (0.05 M) in Me_2SO (K^+, 18-crown-6) yielded a reactivity series for RHgCl of R = $PhCH_2$ (4.7) > Me_3C (1.0) > Me_2CH(0.07) > n-C_6H_{13} (<0.005). However, the possibility of rapid electron transfer between $RHgCl\cdot^-$ and RHgCl cannot be completely excluded at this time. If such a rapid electron transfer process should occur, the apparent relative reactivity of RHgCl would be controlled by the rate of the decomposition of $RHgCl\cdot^-$, a process which reflects the stability of the resulting $R\cdot$. Qualitatively, the presence of an unreactive RHgCl (e.g., n-$C_6H_{13}HgCl$) did not retard the rate of reaction of Me_3HgCl with $Me_2C{=}NO_2^-$, an observation most consistent with a dissociative electron transfer process.

The stability of the radical anion formed in reaction 1 is important in determining if the $S_{RN}1$ process will occur. Thus, with anions such as $(EtO)_2PO^-$ or $(EtO_2C)_2CH^-$, no reactivity towards R• = tert-butyl, n-hexyl, or benzyl is observed under conditions where nitronate anions react readily.[4] Furthermore, in competitive reactions, $Me_2C{=}NO_2^-$ reacts without interference from $(EtO)_2PO^-$ or $(EtO_2C)_2CH^-$.

Since the ability to alkylate an enolate or other resonance stabilized anion by an alkyl free radical and particularly by a 3°-alkyl radical appears to be a valuable and unexplored process, we have investigated the reaction of tert-butylmercury chloride with a variety of nucleophiles. Direct nucleophilic substitution of the S_N2-type is an unknown process for the polarized bond in alkylmercury halides ($^{\delta-}R\text{-}Hg^{\delta+}X$).

Table 1 summarizes the yields of the $S_{RN}1$ products obtained in the reaction of Me_3CHgCl with a variety of anions. In addition to nitronate anions ($^-O_2N{=}C(R_1)(R_2)$), it was found that anions derived from phenones ($PhC(O^-){=}C(R_1)(R_2)$) were capable of trapping tert-butyl radicals. Benzylic anions such as $(Ph)_3C{:}^-$, $(Ph)_2CH^-$, fluorenyl$^-$, or Ph_2CCN^- also yielded tert-butylation products. In the case of Ph_2CCN^-, products of both C- and N-alkylation were observed while $Ph_3C{:}^-$ gave substitution at both the alpha and para positions (reactions 4 and 5).



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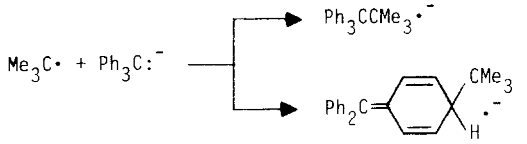


(5)

Among the anions which failed to give at least 3% of the substitution products in 8 h were $HC(NO_2)_2^-$, $C(NO_2)_3^-$, $EtO_2CCPh_2^-$, $Me_3CC(O^-){=}CPh_2$, $MeC(CO_2Et)_2^-$, $PhC(O^-){=}CHCOPh$, $PhC(O^-){=}C(Ph)COPh$, $PhC(O^-)CHCN$, $PhC(O^-)CHCO_2Et$, and 9-nitrofluorene$^-$.

The reactions of Table 1 failed to occur in the dark in the presence of 10 mol % of tert-Bu_2NO•. They would occur in the absence of irradiation at temperatures above 50 °C where the thermolysis of tert-BuHgCl to form Me_3C• becomes important.

To gain a better understanding of the effects which govern the reactivity of a carbanion in this free radical substitution reaction, we have investigated competitive reactions wherein an excess (5-20 equivalents) of $Me_2C{=}NO_2^-$ and a second nucleophile were allowed to react with tert-BuHgCl in a photostimulated or thermal reaction. Competitive reactions were also performed with a 200% excess of tert-BuHgCl in which the reactions were terminated after the consumption of only 3% of the tert-BuHgCl. If ligand exchange was a complicating feature, we expected that a variation in the tert-BuHgCl/nucleophile ratio would cause the observed relative reactivity of the two nucleophiles to vary. This was the case in the competition between $Me_2C{=}NO_2^-$ and $Me_3CC(O^-){=}CH_2$, $PhC(O^-){=}CH_2$, $PhC(CO_2Et)_2^-$, and phthalimide$^-$. For the other nucleophiles for which the relative reactivities are reported, there was no effect of the ratio of tert-BuHgCl/N$^-$ on the observed relative reactivities, and it is believed that the competitive reactions of Scheme 2 are involved.

Table 1. Reaction of nucleophiles with *tert*-BuHgCl[a]

nucleophile[b]	time (h)	product (% yield)[c]
$Me_2C{=}NO_2^-$	2	$Me_3CCMe_2NO_2$ (69)
$MeCH{=}NO_2^-$	2	$Me_3CCH(Me)NO_2$ (74)
$MeC(Ph){=}NO_2^-$	2	$Me_3CC(Me)(Ph)NO_2$ (67)
$H_2C{=}NO_2^-$	2	$Me_3CCH_2NO_2$ (68)
$PhCH{=}NO_2^-$	2	$Me_3CCH(Ph)NO_2$ (71)
NO_2^-	2	Me_3CNO_2 (71)
Phthalimide$^-$ [d]	5	N-*tert*-Butylphthalimide (72)
N_3^- [d]	8	Me_3CN_3 (34)
$PhCHCN^-$	5	$Me_3CH(Ph)CN$ (4) $PhCH_2CMe_3$ (11)
Ph_2CCN^-	2	Me_3CCPh_2CN (48) $Ph_2C{=}C{=}NCMe_3$ (26)
Ph_3C^-	2[e]	Ph_3CCMe_3 (39) 6-*tert*-butyl-3-benzhydrylidene-1,4-cyclohexadiene (21) *p*-$Me_3CC_6H_4CPh_2CMe_3$ (5)
Ph_2CH^-	2[e]	Ph_2CHCMe_3 (36)
Fluorenyl$^-$	2[e]	9-*tert*-Butylfluorene (44)
$PhC(CO_2Et)_2^-$	7	$PhC(CO_2Et)_2CMe_3$ (43)
$Me_3C(O^-){=}CH_2$	8	$Me_3CCOCH_2CMe_3$ (7)
$Me_3C(O^-){=}CPh_2$	6	$Me_3CCOCPh_2CMe_3$ (6)
$PhC(O^-){=}CH_2$	6	$PhCOCH_2CMe_3$ (54)
$PhC(O^-){=}CHMe$	4	$PhCOCH(Me)CMe_3$ (34)
$PhC(O^-){=}CMe_2$	5	$PhCOCMe_2CMe_3$ (21)
$PhC(O^-){=}CHPh$	2	$PhCOCH(Ph)CMe_3$ (63)
$PhC(O^-){=}CPh_2$	2	$PhCOCPh_2CMe_3$ (57)
$PhC(O^-){=}Fl$	8	9-*tert*-butyl-9-benzoylfluorene (8)

[a] Reactions were performed in nitrogen-purged Me_2SO in the presence of equimolar amounts of 18-crown-6, with irradiation from a 275 W sunlamp positioned *ca.* 15 cm from the pyrex reaction flask. [b] Generated by the action of potassium *tert*-butoxide on the conjugate acid. [c] Yields determined by ^1H NMR and GLC on a 1 mmol scale for reactions 0.1 *M* in RHgX and N^-. [d] Commercially available potassium salts were used. [e] HMPA solvent.

$$Me_3CHgCl \xrightarrow{\Delta \text{ or } h\nu} Me_3C\cdot \qquad (6)$$

$$Me_3C\cdot + \begin{array}{l} N_1^- \longrightarrow Me_3C{-}N_1\cdot^- \\ N_2^- \longrightarrow Me_3C{-}N_2\cdot^- \end{array} \qquad (7)$$

$$Me_3{-}N_1\cdot^-,\ Me_3C{-}N_2\cdot^- + Me_3CHgCl \longrightarrow Me_3C{-}N_1,\ Me_3C{-}N_2 + Me_3C\cdot + Hg^\circ + Cl^- \qquad (8)$$

Scheme 2

Table 2 summarizes the competitive data observed in the competitive *tert*-butylation of $Me_2C{=}NO_2^-$ and $PhC(O^-){=}CPh_2$. In Fig. 1 a plot of the ratio of the yields of $Me_3CCMe_2NO_2$ and Me_3CCPh_2COPh as a function of the initial ratio of $Me_2C{=}NO_2^-$ to $PhC(O^-){=}CPh_2$ is given. The linear plot passing through the origin with a slope of 0.46 (r = 0.996) yields a relative reactivity of $PhC(O^-){=}CPh_2$ to $Me_2C{=}NO_2^-$ of 2.2:1.

Table 2. Competitive reaction of Me_3CHgCl with $Me_2C{=}NO_2^-$ and $PhC(O^-){=}CPh_2$[a]

$Me_2C{=}NO_2^-$, *M*	$PhC(O^-){=}CPh_2$, *M*	$Me_3CCMe_2NO_2$ (%)[b]	Me_3CCPh_2COPh (%)[b]
0.06	0.12	17.3 (16.9)	72.1 (70.3)
0.10	0.10	28.6 (27.9)	61.3 (59.8)
0.12	0.06	42.6 (40.5)	46.2 (43.9)
0.12	0.04	50.4 (49.1)	36.7 (35.7)
0.16	0.04	56.2 (55.2)	30.3 (29.8)

[a] See footnotes *a*, *b* of Table 1 for conditions. [b] Yields based on Me_3CHgCl consumed. Yields in parentheses employed excess Me_3CHgCl (0.3 *M*) and were stopped after ~3% reaction (~15 min). The other yields employed 0.01 *M* Me_3CHgCl and were conducted for 1 h during which time the mercurial was essentially completely consumed with 86-90% of the *tert*-butyl fragments accounted for in the alkylation products.

The relative reactivities of a series of carbanions determined by competitive reactions using $Me_2C{=}NO_2^-$ as a standard nucleophile are summarized in Table 3. The absolute rate constant for the trapping of 5-hexenyl radical by $Me_2C{=}NO_2^-$ in Me_2SO at 40 °C is ~2.5×10^5 $M^{-1}s^{-1}$ depending upon the counterion.[3] Presumably, the rate constant for trapping of $Me_3C\cdot$ will be less than that for a 1°-alkyl radical although it is recognized that aliphatic $S_{RN}1$ processes are remarkably insensitive to steric effects.[5] Those anions which were unreactive in the absence of $Me_2C{=}NO_2^-$ not only failed to react in competitive experiments in the presence of $Me_2C{=}NO_2^-$ but failed to interfere with the trapping of $Me_3C\cdot$ by $Me_2C{=}NO_2^-$. A maximum reactivity of not greater than 0.005 that of

$Me_2C{=}NO_2^-$ was observed for $HC(NO_2)_2^-$, $C(NO_2)_3^-$, $Fl{=}NO_2^-$, $Me_3CC(O^-){=}CPh_2$, $HC(CO_2Et)_2^-$, $MeC(CO_2Et)_2^-$, $PhC(O^-){=}CHCOPh$, $PhC(O^-){=}CPhCOPh$, $PhC(O^-){=}CHCN$, $PhC(O^-){=}CHCO_2Et$.

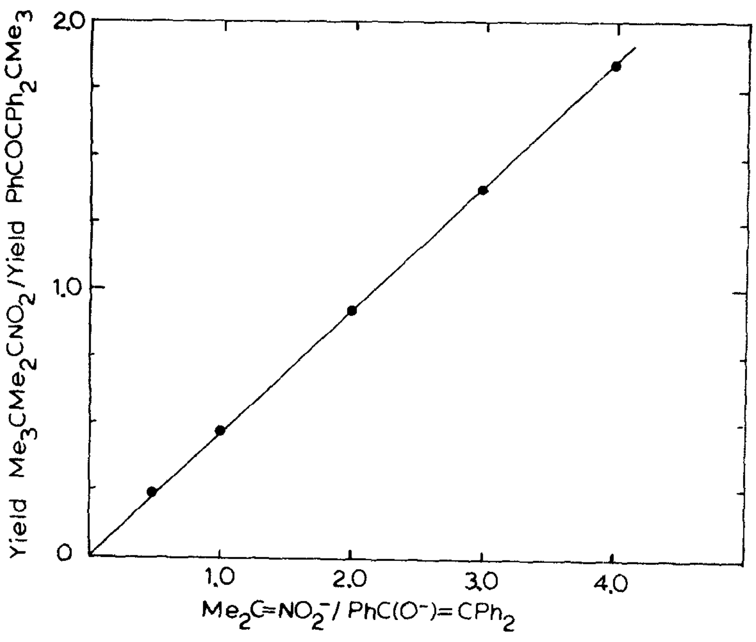


Fig. 1. Ratio of yields ($Me_3CCMe_2NO_2/Me_3CCPh_2COPh$) as a function of $Me_2C{=}NO_2^-/PhC(O^-){=}CPh_2$; $[Me_3CHgCl]_i$ = 0.01 M.

The basicity of the anion would be expected to play an important role in determining the reactivity of an anion with a radical. For a series of anions where the resulting radical anion has a constant stability (e.g., $Me_3CC(R_1)(R_2)NO_2^{\cdot -}$ or $Me_3CC(R_1)(R_2)\dot{C}(O^-)Ph$), the value of $\Delta G°$ for the reaction should increase with the pKa of the conjugate acid of the anion ($\Delta\Delta G° = -1.4\ \Delta pKa$). Thus, if the rate of reaction of a radical with an anion is controlled by the overall change in free energy, the rate should increase with the basicity of the anion if the stability of the radical anion is held constant. This is obviously not the case for many of the entries in Table 3. In Table 4 the pertinent pKa data for the various acetophenone derivatives and calculated $\Delta G°$ values are listed.[6]

Table 4 reveals an inverted reactivity order as a function of pKa, $\Delta G°$, or $\Sigma\sigma^*$ for R_1 and R_2. For the enolate anions of low basicity (R_1, R_2 = H, PhCO; Ph, PhCO; H, CN; H, CO_2Et), the reaction is highly endoergic and no reaction is observed. The reactivity increases sharply from R_1, R_2 = o,o'-biphenylenyl (pKa = 10.1) to $R_1 = R_2$ = Ph (pKa $\cong$ 20), but then the reactivity decreases as the enolate anion is made more basic by the changing R_1 and R_2 from phenyl to methyl or hydrogen. This decrease in reactivity parallels the σ^*-values for the substituents R_1 and R_2 ($\rho = 1.5$).

The tert-butyl radical is a nucleophilic species and prefers to react via a transition state in which an electron has been transferred to the substrate. Apparently the nucleophilicity of the tert-butyl radical becomes the dominant factor for the exoergic reactions of Table 4 where an early transition state is involved. The reactions of nitronate anions seem to follow a similar rate profile. Very weakly basic anions such as $CH(NO_2)_2^-$, $C(NO_2)_3^-$, or $Fl{=}NO_2^-$ fail to trap $Me_3C\cdot$. With R_1, R_2 = H, C_6H_5 ($\Sigma\sigma^* = 1.1$), a lower reactivity is observed than for the more basic $CH_2{=}NO_2^-$ ($\Sigma\sigma^* = 0.98$). However, as the electron donating ability of the substituents increases further, the reactivity now decreases in a linear fashion with $\Sigma\sigma^*$ given $\rho^* = 1.6$ ($r = 0.997$) for $H_2C{=}NO_2^-$, $Me_3CH{=}NO_2^-$, $MeC(Ph){=}NO_2^-$, and $Me_2C{=}NO_2^-$. The same effect seems to occur with acetonitrile derivatives where Ph_2CCN^- is 65 times more reactive than $PhCHCN^-$.

Table 3. Relative reactivity of anions towards $Me_3C\cdot$ at 35 °C in Me_2SO (K^+/18-crown-6)

anions	relative reactivities
$Me_2C{=}NO_2^-$	1.00
$MeCH{=}NO_2^-$	6.1
$H_2C{=}NO_2^-$	35
$PhCH{=}NO_2^-$	1.0
$PhC(Me){=}NO_2^-$	7.4
NO_2^-	0.4
Ph_2CCN^-	6.5
$PhCHCN^-$	<0.1
$PhC(O^-){=}CHMe$	0.20
$PhC(O^-){=}CMe_2$	0.03
$PhC(O^-){=}CHPh$	1.1
$PhC(O^-){=}CPh_2$	2.2
$PhC(O^-){=}Fl$	0.01
Phthalimide$^-$	0.3[a]
$PhC(CO_2Et)_2^-$	0.02[a]

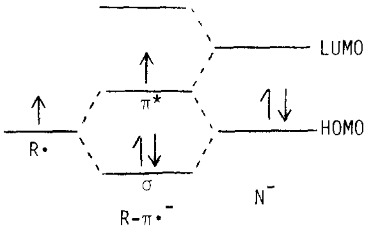
[a] Limiting value at high $[Me_3CHgCl]$ (> 0.3 M) with $[N^-] = [Me_2C{=}NO_2^-] = 0.1$ M.

Competitive thermally initiated reactions of Me_3CHgCl with $Me_2C{=}NO_2^-$ and $MeCH{=}NO_2^-$ were performed at 55-85 °C in the dark. The relative reactivity of $MeCH{=}NO_2^-$ decreased from 5.0 at 55 °C to 4.4 at 65 °C to 4.05 at 75 °C and 3.8 at 85 °C. These data yielded $\Delta H^\ddagger(Me_2C{=}NO_2^-)-\Delta H^\ddagger(MeCH{=}NO_2^-) = 2.2$ kcal/mol, $\Delta S^\ddagger(Me_2C{=}NO_2^-)-\Delta S^\ddagger(MeCH{=}NO_2^-) = 3.6$ e.u. Extrapolation to 35 °C yields $\Delta G^\ddagger(Me_2C{=}NO_2^-)-\Delta G^\ddagger(Me_2CH{=}NO_2^-) = 1.1$ kcal/mol and a calculated relative reactivity of $MeCH{=}NO_2^-$ of 6.2 vs. the photostimulated value of 6.1.

The reaction of a radical with an anion to form a new σ-bond and a radical anion of the π-system appears to be a simple process. However, the reactivity data of Table 4 suggests a fairly complex effect of structure upon rate. An early transition state in the reaction between $Me_3C\cdot$ and N^- may resemble $Me_3C^+\ N\cdot^{2-}$, i.e., a transition state in which the electron has been transferred from the radical to the LUMO of the resonance stabilized anion. In any event, in the reaction an electron must be promoted to a new π^* orbital derived from the LUMO of the anion, Scheme 3. As the basicity of anion increases, the energy levels of the HOMO and LUMO will increase. The exoergicity of the reaction will also increase for a series of similar anions because the energy levels of the σ and π^* orbitals in $R\text{-}\pi\cdot^-$ are independent of the substituents in N^-. However, $\Delta \underline{G}^{\ddagger}$ will not necessarily decrease with an increase in the basicity of the anion if the formation of the σ-bond lags behind the promotion of the unpaired electron to the LUMO of N^-. Phenyl substituents would be expected to lower the energy of LUMO consistent with the reactivity orders of $PhC(O^-)=C(R_1)(R_2)$ > $Me_3CC(O^-)=C(R_1)(R_2)$ or $PhC(O^-)=CPh_2$ > $PhC(O^-)=CMe_2$.

Table 4. Reaction of $Me_3C\cdot$ with $PhC(O^-)=C(R_1)(R_2)$ to yield $Ph\dot{C}(O^-)C(R_1)(R_2)CMe_3$

R_1	R_2	p$\underline{K}$a	$\Delta\underline{G}°$	$\Sigma\sigma^*_{R_1,R_2}$	rel. reactivity
H or Ph	PhCO	~9	-16	2-3	<0.005
o,o'-biphenylenyl(Fl)		10.1	14.4	-1.4	0.01
Ph	Ph	---	---	1.2	2.2
H	Ph	21.5	-1.6	1.1	1.1
H	Me	24.4	-6.4	0.5	0.2
Me	Me	26.3	-8.6	0	0.03



Scheme 3

Methyl radicals are less nucleophilic than tert-butyl radicals. However, in reaction with $Me_2C=NO_2^-$, $MeCH=NO_2^-$, and $H_2C=NO_2^-$, a σ^* correlation with ρ = 1.8 is observed in H_2O vs. the value of ρ = 1.6 observed in Me_2SO for $Me_3C\cdot$.[7] In a competitive experiment, it has been observed that $Ph_3C:^-$ is more reactive than the less basic p-$PhC_6H_4CPh_2^-$ although the exoergicity of the trapping reaction should be considerably greater for the biphenyl derivative because of the stability of the resulting radical anion.[8] In these early transition state reactions, there is a parallel with the $Me_3C\cdot$ reactivity data in that reactivity decreases with an increase in exoergicity although in the series $PhC(O^-)=CPh_2$ > $PhC(O^-)=CMe_2$; $CH_2=NO_2^-$ > $Me_2C=NO_2^-$; $PhCCN^-$ > PhCHCN, the more reactive anion is the least basic. Complete electron transfer over long distances is known to show an inverted reactivity order with the rate first increasing and then decreasing as the exoergicity of the reaction increases.[9] A similar decrease in reactivity with an increase in exoergicity is noted in the trapping of resonance stabilized carbocation by nucleophiles where the reactivity series $N_3^- > HO^- > CN^-$ parallels neither the basicity ($HO^- > CN^- > N_3^-$) nor the exoergicity ($HO^- \sim CN^- > N_3^-$) series but does parallel the ease of oxidation of the nucleophile.[10,11] For the reactivity series of Table 4, there seems to be no overall correlation of reactivity with the ease of oxidation of the nucleophile. The high reactivity of Ph_2CCN^- and $PhC(O^-){=}CPh_2$ is consistent with electron transfer to form $Ph_2\dot{C}CN$ or $PhCO\dot{C}Ph_2$, but on the other hand $Me_3CC(O^-){=}CPh_2$ or $EtOC(O^-){=}CPh_2$ show no reactivity. Complete electron transfer by some mechanism such as Scheme 4 seems to be

$$Me_3CHgCl + R{:}^- \longrightarrow Me_3C\cdot + Hg^\circ + Cl^- + R\cdot$$

$$R\cdot + Me_3C\cdot \longrightarrow RCMe_3,\ R{-}R,\ Me_3C{-}CMe_3$$

Scheme 4

excluded since there is no evidence for the formation of dimers such as $Ph_2C(CN)C(CN)Ph_2$ or $PhCOCH(Ph)CH(Ph)COPh$ which are formed in high yields from Ph_2CCN^- and $PhCOCHPh^-$ by one-electron oxidations (e.g., by $ClCMe_2NO_2$).[12] Furthermore, the observed relative reactivities are independent of the concentration of Me_3CHgCl excluding a competition between the reactions of Schemes 1 and 4.

A reaction mechanism involving the coupling of radicals, e.g., Scheme 4, can also be excluded since the reaction of $Ph_3C\cdot$ or $Ph_2\dot{C}CN$ with an alkyl radical yields exclusively coupling at the benzylic position; the observed para coupling for $Ph_3C{:}^-$ and N-coupling for Ph_2CCN^- are characteristic of radical-anion interactions rather than radical-radical couplings. The coupling of radicals is apparently involved in the process which occurs when Me_3CHgCl is first treated with Me_3COK in Me_2SO and the resulting precipitate of $Me_3CHgOCMe_3$ allowed to react with Ph_3CH with sunlamp irradiation (reactions 9 and 10).

$$\begin{array}{ccccccc} Me_3CHgCl & + & Me_3COK & + & Ph_3CH & \xrightarrow[h\nu,\ 2\ h]{Me_2SO\ (10\ mL)} & Ph_3CCMe_3 \\ 0.1\ mmol & & 0.1\ mmol & & 0.3\ mmol & & 0.07\ mmol \end{array} \qquad (9)$$

$$\begin{array}{ccccccc} Me_3CHgCl & + & Me_3COK & + & Ph_2CHCN & \xrightarrow[h\nu,\ 2\ h]{Me_2SO\ (10\ mL)} & \\ 0.145\ mmol & & 0.125\ mmol & & 0.1\ mmol & & \end{array}$$

$$\begin{array}{ccc} Ph_2C(CN)CMe_3 & + & Ph_2C(CN)C(CN)Ph_2 \\ 0.012\ mmol & & 0.014\ mmol \end{array} \qquad (10)$$

These reactions may occur by the mechanism of Scheme 5.

$$\begin{aligned}
&Me_3CHgOCMe_3 \xrightarrow{\Delta \text{ or } h\nu} Me_3C\cdot + Hg^\circ + Me_3CO\cdot \\
&Me_3CO\cdot + RH \longrightarrow Me_3COH + R\cdot \\
&2\ Ph_2\dot{C}CN \longrightarrow Ph_2C(CN){-}C(CN)Ph_2 \\
&2\ Ph_3C\cdot \rightleftharpoons \text{dimers} \\
&R\cdot + Me_3C\cdot \longrightarrow Me_3CR
\end{aligned}$$

Scheme 5

Scheme 3 describes the reaction of a localized radical with a delocalized anion. For the reverse situation where the radical itself contains a LUMO which may yield the π^* orbital of the radical anion, the available experimental evidence indicates little effect of structure upon the reactivity of those anions which are trapped by the radical. The 2-nitro-2-propyl radical adds to anions such as $(EtO)_2PO^-$ or $MeC(CO_2Et)_2^-$ which have no measurable reactivity towards $Me_3C\cdot$.[13] In competitive reactions, a rate difference of only 10-fold is observed for the series $MeC(CO_2Et)_2^- \sim HC(CO_2Et)_2 > Me_2C{=}NO_2^-$, $(EtO)_2PO^-$, $(EtO)_2PS^-$ toward $Me_2\dot{C}NO_2$.[13] Moreover, when the anion is easily oxidized, e.g., benzylic, the preferred reaction pathway becomes one of electron transfer rather than addition (reaction 11).[12]

$$Me_2\dot{C}NO_2 + PH_2CCN^- \longrightarrow Me_2C{=}NO_2^- + Ph_2\dot{C}CN \qquad (11)$$

EXPERIMENTAL

Alkylation Procedure. Solutions of the nucleophile (N^-) were prepared immediately before use from vacuum dried commercial salts (KNO_2, NaN_3, potassium phthalimide) or by reaction of NH with molar equivalents of Me_3COK and 18-crown-6 under nitrogen. After deoxygenation by nitrogen bubbling for 15-30 min, the Me_3CHgCl[14] was added. Irradiated experiments employed a 275 W sunlamp ca. 15 cm from the pyrex flask. For dark reactions, the flask was wrapped with aluminum foil. Product isolation involved treatment with 50-100 mL of 10% aq NaCl or 5% hydrochloric acid followed by Et_2O extraction. Yields of products were obtained by GLC or ^1H NMR analysis of the concentrated Et_2O extracts using internal standards. The analytical procedures were calibrated with pure samples of the reaction products isolated by distillation, crystallization, or column chromatography.

Competitive alkylations. Standard solutions of N^- and $Me_2C{=}NO_2^-$ in dry, deoxygenated Me_2SO were prepared by the reaction of NH with molar equivalents of Me_3COK and 18-crown-6. Aliquots of the standard solutions were mixed under nitrogen and Me_3HgCl in Me_2SO added. The stirred solutions were irradiated with a 275 W sunlamp for appropriate periods of time determined in preliminary experiments. Concentrated ethereal extracts of the reaction products were analyzed by ^1H NMR (60 MHz) in $CDCl_3$ using CH_2Br_2 or Me_2SO as internal standards or by GLC using $PhCH_2OPh$ or phthalide as standard. Table 2 and Fig. 1 are representative of the competitive experiments which were performed so that the ratio of $[N^-]/[Me_2C{=}NO_2^-]$ remained constant. Reactions were performed with $[Me_3CHgCl] = 0.01$ and 0.3 M at nucleophile concentrations of 0.05-0.20 M. Plots of yield $Me_3C{-}N$/yield $Me_3CCMe_2NO_2$ vs. $[N^-]/[Me_2C{=}NO_2^-]$ were linear ($r = 0.996-0.999$) with a zero intercept except as below.

Competition of $Me_2C=NO_2^-$ and $PhC(O^-)=CH_2$ with a deficiency of Me_3CHgCl failed to produce $Me_3CCMe_2NO_2$. However, with excess Me_3CHgCl, $Me_3CCMe_2NO_2$ was formed. In these reactions, ligand exchange may have occurred to form Me_3CHgCH_2COPh. Phthalimide$^-$ and $PhC(CO_2Et)_2^-$ gave a variable reactivity relative to $Me_2C=NO_2^-$ as the concentration of Me_3CHgCl was varied. However, with $[Me_3CHgCl] > 0.3$ *M* and $[N^-] = [Me_2C=NO_2^-] = 0.1$ or 0.3 *M*, a constant relative reactivity was observed if the reaction was terminated after 3% of the mercurial had been consumed. Ligand exchange or reversibility of the radical trapping step may be involved.

2-Methyl-2-nitropropane. Reaction of 10 mmol of Me_3CHgCl, KNO_2, and 18-crown-6 in 60 mL of Me_2SO with sunlamp irradiation had an induction period of ~10 min after which Hg° precipitated from the solution. After 2 h, the solution was decanted from the Hg drop and added to 50 mL of 10% aq NaCl. The Et_2O extract was washed with aq $Na_2S_2O_3$ (to remove unreacted mercurial), dried over $MgSO_4$, and distilled to give 0.72 g (70%) of Me_3CNO_2, bp 127-128 °C (lit.[15] bp 127 °C); ^1H NMR ($CDCl_3$) δ 1.55 (s); IR (neat) 2980, 1540, 1470, 1395, 1370, 1345, 1250, 1180, 930, 850 cm^{-1}; *m/e* 57.07023 (90), 41 (100) (calc for C_4H_9 ($M^+ - NO_2$): 57.07047). The above experiment when performed in the dark for 4 h did not yield any of the alkylation product. With 10 mol of (*tert*-Bu)$_2$NO•, only 4% of Me_3CNO_2 was formed with sunlamp irradiation for 2 h.

2,3,3-Trimethyl-2-nitrobutane. The photostimulated reaction of Me_3CHgCl, $Me_2C=NO_2^-K^+$, and 18-crown-6 in Me_2SO for 2 h yielded by column chromatography (C_6H_6 (25%)-petroleum ether (75%)), 0.94 g (65%) of $Me_3CCMe_2NO_2$; ^1H NMR ($CDCl_3$) δ 1.05 (s, 9), 1.54 (s, 6); IR (neat) 1550, 1395, 1370, 1350, 930, 850 cm^{-1}; *m/e* 99.11793 (10), 83 (5), 69 (6), 57 (100) (calc for C_7H_{15} ($M^+ - NO_2$): 99.11745). Under the conditions employed, the reactions in the dark did not yield any alkylated product while irradiation in the presence of 10 mol % (*tert*-Bu)$_2$NO• only 3% of $Me_3CCMe_2NO_2$ was detected.

3,3-Dimethyl-2-nitrobutane. Pure material was obtained by column chromatography; ^1H NMR ($CDCl_3$) δ 1.10 (s, 9), 1.55 (d, 3), 4.55 (q, 1); IR (neat) 2990, 1540, 1390, 1365, 1350, 1250, 930, 860 cm^{-1}; *m/e* 85.10204 (calc for C_6H_{12} ($M^+ - NO_2$): 85.10179).

2,2-Dimethyl-1-nitropropane. Reaction on a 10 mmol scale gave 0.8 g (68%) of $Me_3CCH_2NO_2$, bp 145-146 °C; ^1H NMR ($CDCl_3$) δ 1.10 (s, 9), 4.25 (s, 2); IR (neat) 2995, 1550, 1470, 1395, 1370, 1345, 1245, 1175, 930, 850 cm^{-1}; *m/e* 71.08650 (66), 55 (100) (calc for C_5H_{11} ($M^+ - NO_2$): 71.08613).

2,2-Dimethyl-1-phenyl-1-nitropropane. Reaction on a 10 mmol scale of Me_3CHgCl, $PhCH=NO_2^-K^+$, and 18-crown-6 in 60 mL of Me_2SO gave a 71% yield of $Me_3CCH(Ph)NO_2$ after 2 h irradiation. Pure material was obtained by column chromatography (C_6H_6 (33%)-petroleum ether (67%)); ^1H NMR ($CDCl_3$) δ 1.15 (s, 9), 5.72 (s, 1), 7.1-7.6 (m, 5); IR (nujol) 1540, 1350, 740, 695 cm^{-1}; *m/e* 147.11793 (44), 105 (76), 91 (100), 69 (21), 57 (27) (calc for $C_{11}H_{15}$ ($M^+ - NO_2$): 114.11745). With 10 mol % (*tert*-Bu)$_2$NO•, the irradiated reaction gave only 4% of the alkylation product.

3,3-Dimethyl-2-phenyl-2-nitrobutane. A photostimulated reaction of 5 mmol of Me_3CHgCl, $PhC(CH_3)=NO_2^-K^+$, and 18-crown-6 in 30 mL Me_2SO for 2 h gave 0.74 g of crude product from which pure $Me_3CC(Ph)(Me)NO_2$ was isolated by column chromatography using C_6H_6 (50%)-petroleum ether (50%); ^1H NMR ($CDCl_3$) δ 1.10 (s, 9), 1.60 (s, 3), 7.1-7.55 (m, 5); IR (nujol) 1550, 1390, 1370, 1347, 925, 740, 690 cm^{-1}; *m/e* 161.13387 (calc for $C_{12}H_{17}$ ($M^+ - NO_2$): 161.13311). Reaction did not occur in the dark, and only 6% of alkylated product was formed in 2 h in the presence of 10 mol % of (*tert*-Bu)$_2$NO•.

3,3-Dimethylbutyrophenone. Irradiation of 5 mmol of Me_3HgCl, $PhCOCH_2^-K^+$, and 18-crown-6 in 30 mL Me_2SO for 6 h gave 0.47 g (54%) of $PhCOCH_2CMe_3$, bp 114-116 °C (10 torr); ^1H NMR ($CDCl_3$) δ 1.0 (s, 9), 2.95 (s, 2), 7.3-7.5 (m, 3), 7.8-8.0 (m, 2); IR (neat) 3100, 1690, 1675, 1580, 1450, 1390, 1365, 1280, 1160, 1090, 970, 760, 695 cm^{-1}; *m/e* 176.12044 (7), 120 (59), 105 (100), 77 (53), 57 (20) (calc for $C_{12}H_{16}O$ (M^+): 176.12018). The above reaction in the presence of 10 mol % of (*tert*-Bu)$_2$NO• gave 38% of $PhCOCH_2CMe_3$.

2,3,3-Trimethylbutyrophenone. Reaction of $PhC(O^-)=CHMe$ on a 10 mmol scale with 4 h irradiation in 30 mL Me_2SO gave 34% of $PhCOCH(Me)CMe_3$, bp 79 °C (0.5 torr); ^1H NMR ($CDCl_3$) δ 1.0 (s, 9), 1.16 (d, 3), 3.4 (q, 1), 7.4 (m, 3), 7.9 (m, 2); IR (neat) 1680, 1388, 1370, 915 cm^{-1}; *m/e* 190.13626 (1.7), 134 (40), 105 (100), 77 (36), 57 (32) (calc for $C_{13}H_{18}O$

(M^+): 190.13584). In the presence of 10 mol % (*tert*-Bu)$_2$NO$\cdot$, the above reaction gave only 2% of PhCOCH(Me)CMe$_3$ in 4 h of irradiation.

2,2,3,3-Tetramethylbutyrophenone. A reaction on a 10 mmol scale of PhC(O$^-$)=CMe$_2$ with 5 h irradiation gave 21% of PhCOCMe$_2$CMe$_3$[16] purified by GLC (1/4" X 20' 20% OV-3 column, 170 °C); ^{1}H NMR (CDCl$_3$) δ 1.05 (s, 9), 1.15 (s, 6), 7.3-7.4 (m, 3), 7.8-7.9 (m, 2); IR (neat) 3050, 1678, 1385, 1370, 980, 790, 700 cm^{-1}; *m/e* 204.15254 (calc for $C_{14}H_{20}O$ (M^+): 204.15150). In the presence of 10 mol % (*tert*-Bu)$_2$NO$\cdot$, the above reaction did not give a detectable yield (< 3%) of PhCOCMe$_2$CMe$_3$.

3,3-Dimethyl-2-phenylbutyrophenone. A 5 mmol scale reaction of PhC(O$^-$)=CHPh in 30 mL Me$_2$SO with 2 h irradiation gave a 63% yield of PhCOCH(Ph)CMe$_3$ which was recrystallized from ethanol to give 0.78 g of product, mp 55 °C (lit.[17] mp 55-56 °C); ^{1}H NMR (CDCl$_3$) δ 1.08 (s, 9), 4.45 (s, 1), 7.10-8.00 (m, 10); *m/e* 252 (M^+) (0.1), 196 (54), 105 (100) 91 (23), 77 (35), 57 (9). In the presence of 10 mol % (*tert*-Bu)$_2$NO$\cdot$, only 3% of PhCOCH(Ph)CMe$_3$ was formed in 2 h of irradiation.

3,3-Dimethyl-2,2-diphenylbutyrophenone. Irradiation of a 10 mmol scale reaction in 60 mL of Me$_2$SO for 2 h gave 57% of PhCOCPh$_2$CMe$_3$ isolated by column chromatography (benzene (50%)-CHCl$_3$ (50%)), mp 78-79 °C; ^{1}H NMR (CDCl$_3$) δ 1.20 (s, 9), 7.4-8.0 (m, 15); *m/e* 328.18357 (1.2), 223 (100), 165 (6.7), 105 (32), 57 (4.3) (calc for $C_{24}H_{24}O$ (M^+): 328.18282). In the presence of 10 mol % (*tert*-Bu)$_2$NO$\cdot$, only 2% of the alkylated product was observed.

N-tert-Butylphthalimide. Reaction on a 5 mmol scale of Me$_3$CHgCl, potassium phthalimide, and 18-crown-6 in 30 mL Me$_2$SO for 5 h gave after hydrolysis with 10% aq NaCl, Et$_2$O extraction, and recrystallization from hexane 0.73 g (72%) of N-*tert*-butylphthalimide, mp 58-59 °C (lit.[18] mp 59-60 °C); ^{1}H NMR (CDCl$_3$) δ 1.35 (s, 9), 7.65-7.82 (m, 4); IR (KBr) 3030, 1790, 1720, 1450, 1390, 1350, 1210, 1050, 895, 875, 710, 675 cm^{-1}; *m/e* 203 (M^+) (15), 188 (100), 160 (50), 145 (20), 115 (20). In the presence of 10 mol % (*tert*-Bu$_2$NO$\cdot$, the above reaction gave one 3% of the alkylated product.

2-Azido-2-methylpropane. The reaction on a 10 mmol scale of NaN$_3$, Me$_3$CHgCl, and 18-crown-6 in 60 mL Me$_2$SO gave after 8 h irradiation 0.34 g (34%) of Me$_3$CN$_3$, bp 85-87 °C (lit.[19] bp 85-95 °C); ^{1}H NMR (CDCl$_3$) δ 1.52 (s, 9); IR (neat) 3448, 2535, 2095, 1278, 928 cm^{-1}; *m/e* 99 (M^+) (9), 57 (100), 41 (88), 39 (29). In the presence of 10 mol % (*tert*-Bu)$_2$NO$\cdot$, Me$_3$CN$_3$ could not be detected after 8 h of irradiation.

Diethyl phenyl-tert-butylmalonate. A 10 mmol scale reaction of PhC(CO$_2$Et)$_2$$^-K^+$, 18-crown-6, and Me$_3$CHgCl in 60 mL Me$_2$SO for 7 h with sunlamp irradiation gave the alkylated product in 43% yield isolated by column chromatography (C$_6$H$_6$ (67%)- CHCl$_3$ (33%)); ^{1}H NMR (CDCl$_3$) δ 1.2 (t, 6), 1.4 (s, 9), 4.1 (q, 4), 7.15-7.5 (m, 5); IR (nujol) 3060, 3030, 1740, 1600, 1585, 1465, 1390, 1370, 1305, 1273, 1214, 1155, 860, 730, 700 cm^{-1}; *m/e* 292.16795 (3), 236 (5), 219 (6), 163 (10), 135 (13), 91 (25), 57 (100) (calc for $C_{17}H_{24}O_4$ (M^+): 292.16752). In the presence of 10 mol % (*tert*-Bu)$_2$NO$\cdot$, the above reaction yielded < 2% of the alkylated product.

2,2-Dimethyl-1,1-diphenylpropionitrile and N-tert-butyldiphenylketenimine. A 10 mmol reaction of Ph$_2$CCN$^-$K$^+$, 18-crown-6, and Me$_3$CHgCl were irradiated in 60 mL Me$_2$SO for 2 h. The C and N alkylation products could not be separated by distillation but were resolved by GLC (1/4" X 20' 20% OV-3, 250 °C). 2,2-Dimethyl-1,1-diphenylpropionitrile had ^{1}H NMR (CDCl$_3$) δ 1.25 (s, 9), 7.20-7.65 (m, 10); IR (KBr) 3020, 2240, 1600, 1490, 1390, 1365, 920, 730, 690 cm^{-1}; *m/e* 249.15213 (0.1), 234 (1.5), 193 (100), 165 (30), 57 (76) (calc for $C_{18}H_{19}N$ (M^+): 249.15187). The red N-*tert*-butyldiphenylketenimine had ^{1}H NMR (CDCl$_3$) δ 1.4 (s, 9), 7.2-7.6 (m, 10); IR (KBr) 3200, 2800, 2010, 1390, 1370, 765, 690 cm^{-1}; *m/e* 249 (M^+) (19), 234 (100), 193 (5), 165 (12), 116 (91), 89 (33), 77 (11). In the presence of 10 mol % (*tert*-Bu)$_2$NO$\cdot$, neither of the reaction products were observed in a 2 h irradiation period.

Reaction of Me$_3$CHgCl with the anion of phenylacetonitrile. A 10 mmol scale reaction of PhCH$_2$CN, KOCMe$_3$, and 18-crown-6 with Me$_3$CH$_2$Cl in 60 mL of Me$_2$SO under sunlamp irradiation for 5 h gave 4% of 2,2-dimethyl-1-phenylpropionitrile identified by GCMS and 11% of 2,2-dimethyl-1-phenylpropane. Distillation gave 0.15 g (10%) of PhCH$_2$CMe$_3$, bp 75-

77 °C (20 torr), lit.[20] bp 75-76 °C (20 torr); ^{1}H NMR (CDCl$_3$) δ 0.9 (s, 9), 2.43 (s, 2), 7.1 (s, 5).

9-tert-Butylfluorene. A 10 mmol scale reaction of fluorene, Me$_3$COK, 18-crown-6, and Me$_3$CHgCl in 60 mL HMPA was irradiated for 2 h. GC and ^{1}H NMR indicated the formation of 9-*tert*-butylfluorene (44%) and undetermined amounts of bifluorenyl and bifluorenylidene. Preparative GLC (1/4" X 20' 20% OV-3, 250 °C) gave pure 9-*tert*-butylfluorene mp 99-100 °C (lit.[21] mp 101.5 °C); ^{1}H NMR (CDCl$_3$) δ 0.9 (s, 9), 3.95 (s, 1), 7.3-7.9 (m, 8); *m/e* 224 (M$^+$) (0.3), 208 (1), 167 (100), 165 (24), 152 (13), 115 (6), 57 (30). The *tert*-butylation product was not observed in the presence of 10 mol % (*tert*-Bu)$_2$NO•.

2,2-Dimethyl-1,1-diphenylpropane. The mercurial (10 mmol) was added to the red solution from the reaction of 10 mmol of Me$_3$COK and Ph$_2$CH$_2$ in 60 mL HMPA and irradiated for a 2 h period. GLC and ^{1}H NMR indicated the formation of 2,2-dimethyl-1,1-diphenylpropane (36%) and an undetermined amount of Ph$_2$CHCHPh$_2$. Column chromatography (C$_6$H$_6$ (33%)-petroleum ether (67%)) gave Ph$_2$CHCMe$_3$, mp 54-55 °C (lit.[22] mp 55-56 °C); ^{1}H NMR (CDCl$_3$) δ 1.1 (s, 9), 4.3 (s, 1), 7.1-7.6 (m, 10); *m/e* 224 (M$^+$) (0.5), 209 (1.3), 168 (41), 167 (100), 152 (13), 91 (8.5), 77 (3.6), 57 (25). With 10 mol % (*tert*-Bu)$_2$NO•, Ph$_2$CHCMe$_3$ was not detected.

Reaction of Me$_3$CHgCl with Ph$_3$C$^-$K$^+$. The mercurial (10 mmol) was added to the red solution of 10 mmol of Ph$_3$CH, Me$_3$COK, and 18-crown-6 in 60 mL HMPA and irradiated for 2 h. Analysis by ^{1}H NMR and GCMS indicated the formation of Ph$_3$CCMe$_3$ (39%), 6-*tert*-butyl-3-benzhydrylidene-1,4-cyclohexadiene (21%) and *p*-Me$_3$CC$_6$H$_4$CPh$_2$CMe$_3$ (5%). Separation by preparative GLC (1/4" X 20' 20% OV-3, 260 °C) gave pure samples of Ph$_3$CCMe$_3$ and the cyclohexadiene. Ph$_3$CCMe$_3$ had mp 183-184 °C (lit.[23] mp 185 °C); ^{1}H NMR (CDCl$_3$) δ 1.32 (s, 9), 7.1-7.6 (m, 15); *m/e* 300.18821 (11), 285 (30), 243 (67), 165 (100), 91 (37) (calc for C$_{23}$H$_{24}$ (M$^+$): 300.18792).

6-*tert*-Butyl-3-benzhydrylidene-1,4-cyclohexadiene had ^{1}H NMR (CDCl$_3$) δ 1.45 (s, 9), 3.55 (s, 1), 7.0-7.55 (m, 14); *m/e* 300 (M$^+$) (14), 243 (58), 207 (69), 192 (48), 165 (100), 91 (82), 57 (32). The third reaction product, *p*-Me$_3$CC$_6$H$_4$CPh$_2$CMe$_3$, was identified by GCMS giving *m/e* 356 (M$^+$) (2.5), 341 (10), 299 (50), 178 (12), 165 (37), 135 (16), 91 (19), 57 (100). No alkylation products were observed in the presence of 10 mol % (*tert*-Bu)$_2$NO•.

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