tert-Butylation of α,β-Unsaturated Nitriles by *tert*-Butylmercury Halides in the Presence of Iodide Ion[1]

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Abstract: Iodide ion promotes the free radical addition of *t*-BuHgI to acrylonitrile to form *t*-BuCH$_2$CH(CN)HgI. A facile reaction of the adduct 1-cyanoalkyl radical with *t*-BuHgI$_2^-$ is indicated. Further promotion is observed in the presence of NH$_4$I or PTSA/KI in a reaction now leading directly to *t*-BuCH$_2$CH$_2$CN. Protonation of the intermediate adduct radical followed by electron transfer from *t*-BuHgI$_2^-$ is postulated. With fumaronitrile reaction of the adduct, radical [*t*-BuCH(CN)C•HCN] with *t*-BuHgI can be promoted by the addition of acids or bases. In the presence of NH$_4$I or PTSA/KI, the reductive alkylation product is formed, while in the presence of DABCO, oxidative alkylation occurs to yield *t*-BuC(CN)=CHCN and *t*-BuC(CN)=C(CN)Bu-*t*. Protonation of [*t*-BuCH(CN)C•HCN] increases the ease of reduction while deprotonation yields an easily oxidized radical anion.

Introduction

Photolysis of alkylmercury halides with CH$_2$=CHP(O)(OEt)$_2$ or CH$_2$=CHSO$_2$Ph forms the 1:1 adducts in a free radical chain reaction involving substitution at mercury by the localized adduct radical (reaction 1).[2]

$$RCH_2CH(EWG)^\bullet + RHgX \rightarrow RCH_2CH(HgX)(EWG) + R^\bullet \quad (1)$$

The adduct mercurials can be protonolized or reduced by NaBH$_4$ to give the reductive alkylation product (reaction 2).

$$RCH_2CH(HgX)(EWG) \xrightarrow[NaBH_4]{H^+ \text{ or}} RCH_2CH_2(EWG) + HgX^+ \text{ (or } Hg^0) \quad (2)$$

With α,β-unsaturated carbonyls or nitriles the resonance-stabilized adduct radicals do not particpate effectively in reaction 1 with X = Cl or I; the adduct radicals now undergo disproportionation/combination as well as telomer formation.[3] However, by use of RHgX/I$^-$ mixtures in Me$_2$SO, rapid reactions occur which after aqueous workup yield the reductive alkylation products.[3,4] The present study was undertaken to ascertain the nature of iodide ion promotion and the effects of acids and bases upon the electron transfer reactions of cyanoalkyl radicals.

We have recently reported that in the presence of excess I$^-$ rapid free radical additions of *t*-BuHgI to CH$_2$=CH(EWG) occur in the dark at room temperature to yield the adduct organomercurials which in the case of EWG = CO$_2$R or CN can be converted to the reductive alkylation products by electrophilic cleavage with NH$_4^+$.[5] The present paper demonstrates that ammonium ion or other proton donors in the presence of I$^-$ further increase the rate of reaction of α,β-unsaturated nitriles in chain reactions forming *t*-BuCH$_2$CH(CN)HgI and *t*-BuCH$_2$CH$_2$CN competitively and which we ascribe to the participation of

Scheme 1

(a) $R^\bullet + CH_2{=}CH(EWG) \rightarrow RCH_2CH(EWG)^\bullet$

$$RCH_2CH(EWG)^\bullet + RHgI_2^- \rightarrow RCH_2CH(HgI_2^-)(EWG) + R^\bullet$$

(b) $RCH_2CHCN^\bullet + H^+ \rightleftharpoons RCH_2CH{=}C{=}NH^{\bullet+}$

$$RCH_2CH{=}C{=}NH^{\bullet+} + RHgI_2^- \rightarrow R^\bullet + HgI_2 + RCH_2CH{=}C{=}NH$$

$$RCH_2CH{=}C{=}NH \rightarrow RCH_2CH_2CN$$

mercurate complexes in the reactions of Scheme 1.

Adduct radicals which do not readily react with RHgI$_2^-$ but are basic (e.g., RCH$_2$NR′• formed by adding R• to CH$_2$=NR′) can be activated by protonation to form the radical cations which are readily reduced by I$^-$ or RHgI$_2^-$.[6] In the case of imines, protonation increases not only the electron affinity of the adduct radical but also the reactivity of the imine in radical addition.[6] However, for reactions of α,β-unsaturated nitriles with *t*-BuHgI/I$^-$, we observe promotion of the chain reaction of Scheme 1b without substrate activation, i.e., the adduct radical but not the substrate is protonated.

Another form of adduct radical activation involves the loss of an acidic proton to yield a radical anion which readily reduces RHgX. This process, previously recognized for β-ketoalkyl radicals[7] and for dihydropyridine-type radical cations,[8] also occurs for β-cyanoalkyl radicals. Thus, with fumaronitrile the addition of *t*-Bu• generates an adduct radical which rather uniquely demonstrates amphoteric behavior in that it can be activated toward electron transfer by either protonation or deprotonation (Scheme 2).

Results and Discussion

Acrylonitrile (AN). Reaction in the dark with *t*-BuHgCl, *t*-BuHgI, (*t*-Bu)$_2$Hg, or (*t*-Bu)$_2$Hg/KI in Me$_2$SO is not observed.

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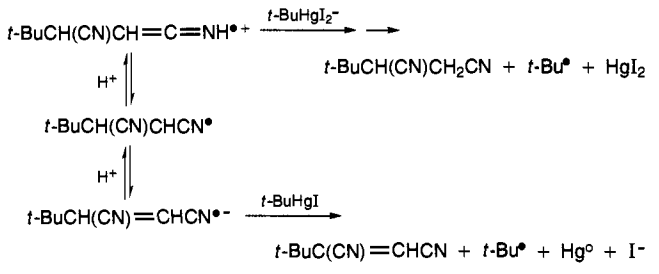
Scheme 2[a]



[a] R = *t*-Bu.

Addition of KI to *t*-BuHgCl or *t*-BuHgI in Me_2SO leads to a rapid reaction with AN in the dark at room temperature. The reactions are typically inhibited by 10 mol % of $(t\text{-Bu})_2NO^\bullet$ for more than 12 h, proving that the dark reactions proceed by a chain initiated by the thermal production of *t*-Bu•. Species such as $t\text{-BuHgI}_2^-$ or $(t\text{-Bu})_2Hg$ may be involved in the initiation process.[3] However, it does not appear that $(t\text{-Bu})_2Hg$ plays a significant role in trapping the adduct radical since $(t\text{-Bu})_2Hg$/KI does not give a significant dark reaction while irradiation gives a complex product mixture.

The reactions with *t*-BuHgI/KI are conveniently monitored by ^1H NMR in Me_2SO-d_6 solution since the signals from *t*-BuHgI, **1**, **2**, and **3** are well separated at δ = 1.4, 0.92, 0.94,

$$t\text{-BuCH}_2\text{CH(CN)HgI} \qquad [t\text{-BuCH}_2\text{CH(CN)}]_2\text{Hg}$$
$$\mathbf{1} \qquad\qquad \mathbf{2}$$

$$t\text{-BuCH}_2\text{CH}_2\text{CN}$$
$$\mathbf{3}$$

and 0.89, respectively. With KI as the iodide source the 1:1 adduct **1** is the initial product (Table 1). This product is formed in the presence of 10 mol % of D_2O consistent with Scheme 1a and excluding a process in which electron transfer forms $t\text{-BuCH}_2\text{CH(CN)}^-$. However, the transition state for the reaction of $t\text{-BuCH}_2\text{CHCN}^\bullet$ with $t\text{-BuHgI}_2^-$ must involve considerable charge transfer, e.g., **4**, a formulation which explains why

$$t\text{-BuCH}_2\text{CH(CN)}^-\text{- - -HgI}_2\text{- -R}^\bullet$$
$$\mathbf{4}$$

$t\text{-BuHgI}_2^-$ is a better trap for the adduct radical than *t*-BuHgI or $(t\text{-Bu})_2Hg$. The initial adduct **1** can be converted in high yield to **3** by protonolysis with NH_4^+/H_2O or by reduction with $NaBH_4$. However, in the absence of these reactions, **1** is converted to the dialkylmercurial **2** in essentially quantitative yield. The mercurial **2** which is not as easily protonated as **1** can be isolated after hydrolysis. The conversion of **1** to **2** is faster with sunlamp irradiation or in the presence of excess *t*-BuHgI and much faster at 40 than at 25 °C. It appears that the comproportionation of **1** can proceed by a radical process as illustrated in Scheme 3.

Scheme 3

$$t\text{-BuCH}_2\text{CHCN}^\bullet + \mathbf{1} \rightleftharpoons \mathbf{2} + \text{I}^\bullet$$

$$\text{I}^\bullet + \mathbf{1} \rightarrow t\text{-BuCH}_2\text{CHCN}^\bullet + \text{HgI}_2$$

In the presence of NH_4I both the adduct mercurial **1** and the reductive alkylation product **3** are observed at short reaction periods. Measurement of the initial ratio of **3**/**1** is complicated by the participation of NH_4^+ in reaction 2. However, extrapolation of the curves of Figure 1 to $t = 0$ clearly demonstrates that the concentration of NH_4I controls the competition between the processes leading to **1** and **3**. As the concentration of NH_4^+ increases the initial ratio of **3**/**1** increases as expected for the competing reactions of Scheme 1. [Both processes should be first order in I^- because of the equilibrium, *t*-BuHgI + $I^- \rightleftharpoons$ $t\text{-BuHgI}_2^-$.] The 1-cyanoalkyl radical apparently has a basicity more characteristic of an imine ($RCH_2CH{=}C{=}\ddot{N}^\bullet$) than of a nitrile ($RCH_2C^\bullet HC{\equiv}N{:}$).

The adduct radical $t\text{-BuCH}_2\text{CHCN}^\bullet$ can also be trapped in a chain reaction by $CH_2{=}CHCH_2Br$.[9] Thus, in PhH solution, photolysis of *t*-BuHgCl, AN, and $CH_2{=}CHCH_2Br$ forms the

Table 1. Reaction of $CH_2{=}CHCN$ (AN) with *t*-BuHgX in Me_2SO-d_6[a]

	mol equiv			% of AN[b]			
AN(M)	*t*-BuHgI	M^+I^-	conditions	RH	RHgI	R_2Hg	AN
0.1	2	KI(2)	5 min, dark	0	17	0	83
0.1	2	KI(2)	15 min, dark	0	32	<2	64
0.1	2	KI(2)	55 min, dark	0	28	34	35
0.1	2	KI(2)	2 h, dark	0	10	80	10
0.1	2	KI(2)	5 h, dark	0	0	100	0
0.1	2	KI(8)	10 min, dark	0	95	5	0
0.1	2	KI(8)	40 min, dark	0	77	23	0
0.1	2	NH_4I(8)	5 min, dark	38	49	13	0
0.1	2	NH_4I(8)	30 min, dark	70	14	16	0
0.1	2	NH_4I(8)	8 h, dark	92	0	8	0
0.1	2	NH_4I(8), D_2O(60)	50 min, dark	80[c]	5	12	0
0.1	4	KI(4)	20 min, dark	0	2	98	0
0.2	2	KI(4)	5 min, dark	0	90	0	10
0.2	2	KI(4)	30 min, dark	0	70	30	0
0.2	2	KI(4)	3.5 h, dark	0	5	95	0
0.2	2	NH_4I(2), KI(6)	5 min, dark	24	67	9	0
0.2	2	NH_4I(2), KI(6)	10 min, dark	27	61	11	0
0.2	2	NH_4I(2), KI(6)	15 min, dark	32	53	15	0
0.2	2	NH_4I(4), KI(4)	5 min, dark	22	40	8	30
0.2	2	NH_4I(4), KI(4)	10 min, dark	30	51	9	10
0.2	2	NH_4I(0.4), KI(4)	15 min, dark	38	48	14	0
0.2	2	NH_4I(8)	5 min, dark	39	41	10	10
0.2	2	NH_4I(8)	10 min, dark	55	38	7	0
0.2	2	NH_4I(8)	15 min, dark	63	27	8	0
0.2	1.1	KI(2 or 8)	10 min, *hν*	0	2	98	0
	1.1	KI(8)	10 min, dark, 40 °C	0	49	39	12
0.2	1.1	KI(8)	30 min, dark, 40 °C	0	18	82	0
0.2	1.1	NH_4I(8)	10 or 20 min, *hν*	95	0	5	0
0.2	1.1	NH_4I(8)	10 min, dark, 40 °C	78	17	5	0
0.2	1.1	NH_4I(8)	30 min, dark, 40 °C	92	4	4	0
0.025	4[d]	NH_4I(20)	12 h, *hν*	95[e]	–	–	–
0.025	4[d]	NH_4I(8)	4 h, *hν*	82[e]	–	–	–
0.025	4[d]	NH_4I(8)	5 h, dark	78[e]	–	–	–
0.025	4[d]	NH_4I(8), D_2O(22)	5 h, *hν*	89[c,e]	–	–	–
0.025	4[d]	KI(8), NH_4Br(8)	5 h, *hν*	95[e]	–	–	–
0.025	4[d]	NH_4Cl(8)	3 h, *hν*	19[e]	–	–	–
0.025	4[d]	KI(8)	40 min, *hν*	21[e]	–	++	–
0.025	4[d]	KI(8)	40 min, *hν*	79[f]	–	+	–
0.025	4[d]	KI(8)	40 min, dark	72[f]	–	+	–
0.025	2[d]	KI(4)	3 h dark	65[g]	–	–	–

[a] At 25 °C for dark reactions, 35−40 °C for reactions irradiated with a 275 W sunlamp. [b] ^1H NMR yield with toluene as an internal standard on a 0.1−0.2 mmol scale; R = $t\text{-BuCH}_2\text{CH(CN)}$. [c] $t\text{-BuCH}_2\text{CH(D)CN}$. [d] *t*-BuHgCl in Me_2SO. [e] After workup with aqueous $Na_2S_2O_3$. [f] Workup by aqueous NH_4I for 1 h before treatment with aqueous $Na_2S_2O_3$ and extraction. [g] Workup with $NaBH_4$.

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(10) In the presence of I^- the allyl bromide is converted to the iodide which reacts readily with radicals by iodine atom abstraction.[9]

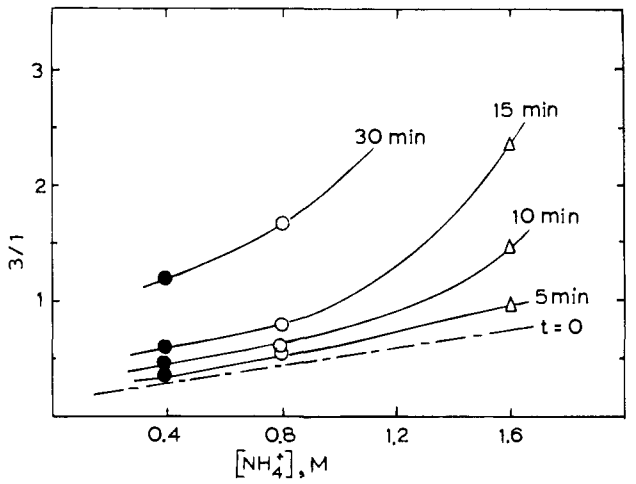


Figure 1. Reaction of 2 equiv of *t*-BuHgI with 0.2 M AN in the presence of 8 equiv of M^+I^- at room temperature in the dark: O, 0.4 M NH_4^+, 1.2 M K^+; ●, 0.8 M NH_4^+, 0.8 M K^+; △, 1.6 M NH_4^+.

Scheme 4

$$t\text{-}BuCH_2CHCN^\bullet + CH_2{=}CHCH_2Br \rightarrow t\text{-}BuCH_2CH(CN)CH_2CH{=}CH_2 + Br^\bullet$$
5

$$Br^\bullet + t\text{-}BuHgI \rightarrow t\text{-}Bu^\bullet + BrHgI$$

$$t\text{-}Bu^\bullet + CH_2{=}CHCN \rightarrow t\text{-}BuCH_2CHCN^\bullet$$

three-component condensation product **5** (Scheme 4).[10]

Photolysis of AN (0.025 M) in the presence of 4 equiv of *t*-BuHgI in Me_2SO-d_6 at 35−40 °C gives a mixture of at least eight different products containing a *tert*-butyl group bound to carbon with the AN completely consumed in 5 h of sunlamp irradiation. Workup with NH_4I/H_2O or $NaBH_4$ gives **3** in ~40%, yield but also detected by GCMS are *t*-$BuCH_2CH(CN)$-$CH(CN)CH_2Bu$-*t* (two isomers), *t*-$BuCH_2CH(CN)Bu$-*t*, and traces of the telomer *t*-$Bu[CH_2CH(CN)]_2H$. Photolysis of **2** prepared by the reaction of AN with 1.1 equiv of *t*-BuHgI/KI occurs slowly. In 8 h the major products are a 1:1 mixture of the two diastereomers *t*-$BuCH_2CH(CN)CH(CN)CH_2$*t*-Bu (33%), 5% of **3**, and 20% of recovered **2**. Bimolecular reactions of *t*-$BuCH_2CHCN^\bullet$ must lead mainly to dimerization with very little disproportionation.

Evidence for Ketenimine Formation. No spectroscopic evidence for *t*-$BuCH_2CH{=}C{=}NH$ formation (Scheme 1b) from AN in the presence of NH_4I has been obtained. In Me_2SO presumably the rearrangement to **3** occurs rapidly in the presence of NH_4^+. However, evidence for an intermediate other than **1** has been observed in proton-promoted reductive alkylations. In the presence of 4 equiv of *p*-toluenesulfonic acid (PTSA·H_2O) the reaction of AN with *t*-BuHgI and KI forms *t*-$BuCH_2CH_2CN$ and *t*-$BuCH_2CH_2CONH_2$ in a ratio of ~1:2 which does not change between 5 and 30 min (all AN consumed in 5 min). Reaction of **2** with PTSA·H_2O (5 equiv) for 24 h at 40 °C fails to form *t*-$BuCH_2CH_2CONH_2$ with only ~25% of **2** converted to **3**. In the presence of PTSA and EtOH the reaction of AN with *t*-BuHgI/KI also forms *t*-$BuCH_2CH_2CO_2Et$. These results are consistent with the formation of *t*-$BuCH_2CH{=}C{=}NH$ followed by acid-catalyzed hydrolysis or ethanolysis. Another observation that appears to call for an intermediate such as the ketenimine concerns the formation of **2** in the NH_4I-promoted system. With KI in the dark at 25 °C the initial product (5 min) formed is exclusively **1** (Table 1). Comproportionation to form **2** occurs slowly in the absence of irradiation at room temperature while reaction of preformed **1** with NH_4I/H_2O forms **3** quantitatively. However, the dark reaction of AN and *t*-BuHgI in the presence of NH_4I forms significant amounts of **2** (8−12%) in a 5 min reaction period at 25 °C. The amount of **2** remains constant as the **1** initially formed is slowly converted to **3** over a period of several hours. The rapid initial formation of **2** (together with **1** and **3**) in the NH_4I-promoted system can be explained by competition between isomerization of *t*-$BuCH_2$-$CH{=}C{=}NH$ to **3** and electrophilic addition of **1** to *t*-$BuCH_2$-$CH{=}C{=}NH$ to form **2** (Scheme 5).

Scheme 5

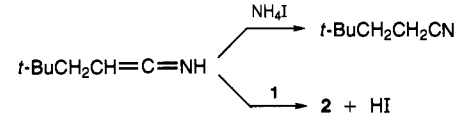


Table 2. Reaction of *t*-BuHgI with 0.2 M Fumaronitrile (FN) in Me_2SO-d_6

t-BuHgI (equiv)	M^+I^- (equiv)	conditions[a]	% of FN[b] RH	% of FN[b] RHgI + R_2Hg
2	KI (8)	50 min, dark	no reaction	
2	NH_4I (8)	50 min, dark	96	−
2	NH_4I (4)	5 min, dark	25	75
1.1	−	5 min, *hν*	no reaction	
1.1	KI (2)	5 min, *hν*	−	>95
1.1	KI (2)	10 min *hν*, 10% $(t\text{-Bu})_2NO^\bullet$	no reaction	
1.1	KI (2)	10 min, *hν*	−	>99
1.1	KI (2)	10 min, *hν*; NH_4I (8), 14 h dark	82	−
1.1	NH_4I (8)	5 min, *hν*	95	−
1.1	NH_4I (8)	10 min, *hν*	99	−
2.0	NH_4I (2)	5 min *hν*; 5 h dark[d]	85	−
2.0[c]	NH_4I (2)	10 h, dark	80[e]	−
2.0[c]	NH_4I (4)	12 h dark, 10% $(t\text{-Bu})_2NO^\bullet$	no reaction	
4.0[c]	NH_4I (8)	100 min, *hν*	99[e]	−

[a,b] See Table 1; R = *t*-BuCH(CN)CHCN. [c] *t*-BuHgCl. [d] Little change between 0.5 and 5 h in dark. [e] After workup with aqueous $Na_2S_2O_3$, $[t\text{-BuHgCl}]_0 = 0.025$ M.

The conversion of **1** to **3** in the presence of NH_4I occurs more rapidly at 40 than at 25 °C and also more rapidly with sunlamp irradiation, e.g., compare the dark and photostimulated reactions with 1.1 equiv of *t*-BuHgI at 40 °C in Table 1. Upon irradiation the main pathway for the **1** → **3** conversion appears to be via Scheme 1b with *t*-$BuCH_2CH(CN)HgI_2^-$ taking the place of *t*-$BuHgI_2^-$. The rapid destruction of **1** in the photostimulated reaction with NH_4I also appears to minimize the formation of **2**.

Methacrylonitrile, α-Chloroacrylonitrile, and Crotononitrile. The tertiary adduct radical formed by addition of *t*-Bu• to methacrylonitrile fails to react readily with *t*-$BuHgI_2^-$. Dark reactions are no longer observed even in the presence of NH_4^+, while photolysis in the presence of NH_4I or KI/PTSA gives a mixture of products including *t*-$BuCH_2C(CH_3)(CN)C(CH_3)$-$(CN)CH_2$*t*-Bu. However, α-chloroacrylonitrile reacts with *t*-BuHgI (5 equiv)/KI (5 equiv)/PTSA (5 equiv) upon photolysis for 24 h to form *t*-$BuCH_2CH(CN)Cl$ in 65% and (*E*)-*t*-$BuCH_2C$-$(CN){=}C(CN)CH_2$*t*-Bu in 13% yield. Photolysis of α-chloroacrylonitrile with 2 equiv of $(t\text{-Bu})_2Hg$ in PhH also produces the 4,5-dicyano-2,2,7,7-tetramethyl-4-octene (~20%), presum-

Table 3. Oxidative and Reductive *tert*-Butylation of Fumaronitrile (FN) in Me_2SO[a]

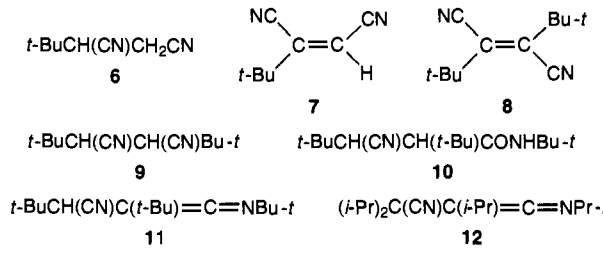
substrate	*t*-BuHgCl (equiv)	KI (equiv)	other	time (h)	b 6	7	8	9	10
FN	2	2	PTSA(2)	23	>95	–	–	–	–
FN	2	2	–	23	44	14	tr	tr	tr
FN	2	0	0	23	tr	–	–	–	–
FN	1	1	DABCO(1)	2	12	82	tr	tr	tr
FN	2	2	DABCO(2)	3	15		31	tr	tr
FN	2	2	DABCO(2)	15	15	tr	56	10	–
FN	2	0	DABCO(4)	2	tr	tr	64	tr	tr
7	5	5	DABCO(5)	2	–	–	60	–	9
7	5	5	PTSA(5)	24	–	–	–	75	8[c]

[a] Photolysis with a 275 W fluorescent sunlamp at 35–40 °C. [b] By ^1H NMR with $PhCH_3$ as an internal standard after workup with aqueous $Na_2S_2O_3$. [c] Traces of *t*-BuCH(CN)CO*t*-Bu observed from the hydrolysis of **7**.

ably by chlorine atom abstraction from *t*-$BuCH_2C(Cl)(CN)$-$C(Cl)(CN)CH_2Bu$-*t* followed by β-elimination of a chlorine atom.

A mixture of the *E*- and *Z*-isomers of crotononitrile reacted with *t*-BuHgI/KI to form the organomercurials or with *t*-BuHgI/NH_4I to form *t*-$BuCH(CH_3)CH_2CN$. Reaction with 2 equiv of *t*-BuHgI and 8 equiv of NH_4I for 4 h at room temperature in the dark gave a 95% yield of the reductive alkylation product with ~5% of the starting crotononitrile present as the organomercurials RHgI and/or R_2Hg with R = *t*-$BuCH(CH_3)CHCN$. As in the case of AN, the initial reaction products were a mixture of RH, RHgI, and R_2Hg in which the organomercurials were slowly converted to RH.

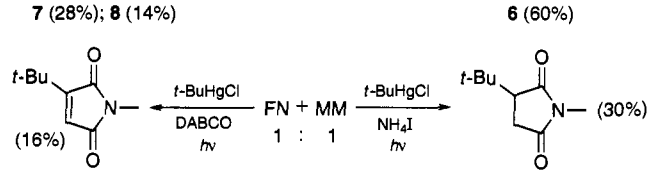
Fumaronitrile (FN). FN does not react as rapidly as AN or crotononitrile with *t*-BuHgI/KI (Table 2). [However, in competitive reactions, FN is ~20 times as reactive as AN toward *t*-Bu•.[3]] With KI as the iodide source no reaction between FN and 2 equiv of *t*-BuHgI was observed in 50 min in the dark at room temperature. Upon photolysis a rapid formation of the organomercurials occurred within 5 min. Workup with aqueous $Na_2S_2O_3$ formed the reductive alkylation product **6** in high yield. Compound **6** is also formed rapidly in the dark by reaction of



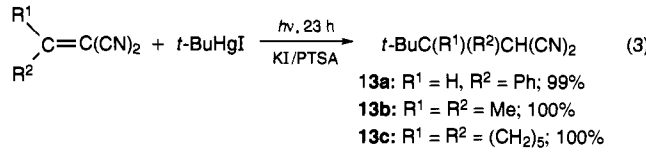
mixtures of *t*-BuHgI with NH_4I or *t*-BuHgCl/KI/PTSA. FN demonstrates a dramatic increase in the overall rate of the reaction by protonation of the adduct radical and promotion of the electron transfer of Scheme 1b.

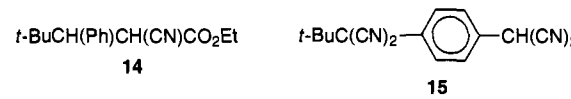
In the presence of DABCO fumaronitrile reacts with *t*-BuHgCl upon photolysis to form the oxidative alkylation products **7** and **8**. Further reaction of **7** with *t*-BuHgCl/KI/PTSA forms **9** and **10** Table 3. Compound **10** appears to be formed by the coupling of *t*-$BuCH(CN)C(t\text{-}Bu)CN$• with *t*-Bu• to yield the ketenimine **11** followed by hydrolysis. Photolysis of FN with *i*-PrHgCl (5 equiv)/KI (10 equiv)/PTSA (3 equiv) for 4 h formed *i*-PrC(CN)=C(CN)Pr-*i* in 67% yield accompanied by the isolable ketenimine **12**. Further photolysis of *i*-PrC(CN)=C-(CN)*i*-Pr with excess *i*-PrHgCl/KI/PTSA for 48 h formed **12** in 83% yield. However, a product analogous to **12** was not detected upon the photolysis of **8** with *t*-BuHgCl/KI.

Scheme 6



1,1-Dicyanoalkenes. Reaction 3 occurred upon sunlamp irradiation in the presence of 4 equiv each of *t*-BuHgI and PTSA. In a similar fashion PhCH=C(CN)CO_2Et was converted to **14** and TCNQ to **15**.





Effect of Proton Donors on the Reactivity of α,β-Unsaturated Nitriles. The reactivities of FN and (dicyanomethylene)-cyclohexane toward *t*-Bu• are not affected by the presence of proton donors. Competition between FN and *N*-methylmaleimide (MM) with a deficiency of *t*-BuHgCl indicates a constant relative reactivity in the presence of NH_4I or DABCO (Scheme 6). In the competitive reductive *tert*-butylation k_{FN}/k_{MM} is 2.5, while the oxidative alkylation in the presence of DABCO gives $k_{FN}/k_{MM} = 2.2$.

Competitive photostimulated *tert*-butylation of (dicyanomethylene)cyclohexane to give **13c** and (*E*)-PhCH=CHI (to give (*E*)-PhCH=CHBu-*t*)[11] by *t*-BuHgI/KI gives a relative reactivity of 1.3 in favor of the nitrile. In the presence of added TMSI/H_2O the relative reactivity is 1.2, while with 1 equiv of PTSA the relative reactivity is 1.6. The promotion by proton donors of the reactions of α,β-unsaturated nitriles with *t*-BuHgX/KI must involve the protonation of the adduct radicals and not the substrates since the relative reactivities of the substrates are not affected by the presence of proton donors.

Conclusions

Proton donors or acceptors will promote the electron transfer reactions of 1-cyanoalkyl or 1,2-dicyanoalkyl radicals. With proton donors as weak as NH_4^+, reductive alkylation via electron transfer from *t*-$BuHgI_2^-$ to the adduct radical is greatly facilitated. On the other hand, the adduct radical from fumaronitrile can be deprotonated by bases such as DABCO to form a radical ion which is a potent reducing species and readily transfers an electron to *t*-BuHgI to yield the oxidative alkylation product. *An increase in the ease of reduction upon protonation and in the ease of oxidation upon deprotonation appears to be a general phenomenon for appropriately substituted alkyl radicals.*

Experimental Section

^1H and ^{13}C NMR spectra were obtained with a Nicolet NT300 spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained with a Finnigan 4000 (INCOS data system) in the GC mode and high-resolution spectra by a Kratos MS-50 spectrometer. Infrared spectra were obtained with a Digital FTS-7FT or IBM IR-98FT spectrometer. Neat spectra were recorded between

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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 (Kiesel gel 60, 230–400 mesh ASTM) usually with hexane (99%)–ethyl acetate (1%). Analytical gas chromatography was performed with a Varian 3700 chromatograph with a Hewlett Packard 3390A integrator employing toluene, naphthalene, or biphenyl as the internal standard. Photostimulated reactions utilized a Sylvania 275 W fluorescent sunlamp and Pyrex reaction vessels at ca. 35–40 °C.

Solvents and Materials. Me_2SO was stirred over CaH_2 for 12 h at 80 °C, distilled, and stored over 4 Å molecular sieves. Alkylmercury halides were prepared according to literature procedures.[12] *tert*-Butylmercury chloride (mp 100–113 °C) was prepared in 50% yield after recrystallization from hexane (90%)–ethanol (10%) by reaction of *t*-BuMgCl with $HgCl_2$ in THF at 0 °C. The mercurial was stored in the absence of light at 0 °C. Di-*tert*-butylmercury (mp 52–55 °C) was prepared by a literature procedure.[13] *t*-BuHgI was prepared by reaction of *t*-BuHgCl (0.03 mol) with KI (0.06 mol) in 50 mL of Me_2SO.[14] After 2 h at 25 °C the solution was treated with 100 mL of water and extracted with Et_2O. After drying over $MgSO_4$ the solvent was evaporated to give white crystals which turned yellow when exposed to air. ^1H NMR ($CDCl_3$): δ 1.54 (s). ^1H NMR (Me_2SO-d_6): δ 1.43 (s). The compound decomposes upon heating and does not give a well-defined mp.

General Procedure for Reactions of RHgCl with Alkenyl Substrates. A Pyrex tube containing RHgX and the substrate in Me_2SO under a positive pressure of N_2 was irradiated at 35–40 °C. The reaction product was treated with aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2. An internal standard, usually toluene, was added and the crude product analyzed by ^1H NMR and/or GC. Reactions in Me_2SO-d_6 were performed in 6 mm NMR tubes on a 0.5 mL scale with toluene as an internal standard.

4,4-Dimethylpentanenitrile (3).[15] ^1H NMR (300 MHz, $CDCl_3$): δ 2.30–2.24 (m, 2 H), 1.63–1.58 (m, 2 H), 0.92 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 127.80, 39.21, 30.35, 28.66, 12.75. GCMS: *m/z* 112 (M + 1^+, 3), 96 (85), 69 (31), 57 (100).

4,4-Dimethylpentanamide.[16] Mp: 140–141 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 6.21 (br s, 1 H), 5.77 (br s, 1 H), 2.22–2.16 (m, 2 H), 1.58–1.52 (m, 2 H), 0.90 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.7, 39.2, 31.5, 30.5, 29.0. GC and HRMS: calcd for $C_7H_{15}NO$ *m/z* 129.1154, found 129.1150 (1.5), 114 (31), 97 (17), 73 (65), 72 (100), 57 (39). FTIR ($CDCl_3$): ν = 3352, 3188 cm^{-1}.

Ethyl 4,4-Dimethylpentanoate.[15] Photolysis of CH_2=CHCN (1 mmol), *t*-BuHgI (2.5 mmol), KI (2.5 mmol) and PTSA·H_2O (2.5 mmol) for 24 h in 10 mL of Me_2SO (50%)–EtOH (50%) followed by workup gave 13% of **3**, 13% of *t*-$BuCH_2CH_2CONH_2$, and 70% of *t*-$BuCH_2CH_2CO_2Et$. ^1H NMR (300 MHz, $CDCl_3$): δ 4.18–4.08 (m, 2 H), 2.30–2.24 (m, 2 H), 1.57–1.52 (m, 2 H), 1.26 (*t*, *J* = 7.2 Hz, 3 H), 0.90 (s, 9 H). GC and HRMS: *m/z* 159 (M + 1^+, 0.5), 158.1325 (M^+, 0.3, calcd for $C_9H_{18}O_2$ 158.1307), 143.1073 (M - 15^+, 21, calcd for $C_{17}H_{13}O$ 113.0967), 102.0684 (M - 56^+, 59, calcd for $C_5H_{10}O_2$ 102.0681), 97 (52), 85 (7), 74 (26), 69 (66), 57 (100). FTIR ($CDCl_3$): ν = 1734 cm^{-1}.

(3,3-Dimethyl-1-cyanobutyl)mercury Iodide (1). This intermediate was detected in Me_2SO-d_6 solution. ^1H NMR (300 MHz): δ 2.28 (dd, *J* = 10.5, 4.0 Hz, 1 H), 1.80 (dd, *J* = 14.2, 4.0 Hz, 1 H), 1.70 (dd, *J* = 14.2, 10.5 Hz, 1 H), 0.92 (s, 9 H).

Bis(1-cyano-3,3-dimethylbutyl)mercury. (1-Cyano-3,3-dimethylbutyl)mercury iodide (**1**) in Me_2SO slowly underwent comproportionation to form the dialkylmercurial. The reaction occurred more rapidly upon sunlamp photolysis and was essentially complete after 30 min of photolysis. Workup with H_2O and CH_2Cl_2 extraction gave the mercurial (mp 168–170 °C) whose ^1H NMR spectrum required a 1:1 mixture of meso and racemic forms. In $CDCl_3$ the methine hydrogen was observed as two dd in a 1:1 ratio although only a single sharp *t*-Bu peak was observed. ^1H NMR (300 MHz, $CDCl_3$): δ 2.259 (dd, *J* = 9.0, 5.7 Hz, 0.5 H), 2.267 (dd, *J* = 9.0, 5.7 Hz, 0.5 H), 2.02 (dd, *J* = 14.1, 9.0 Hz, 1 H), 1.80 (dd, *J* = 14.1, 5.7 Hz, 1 H), 1.02 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.97, 43.32, 32.38, 29.29, 28.93. EIMS (solids sample probe): *m/z* 110 (12), 96 (6), 57 (100). CIMS (NH_3, solids sample probe): calcd for M + NH_4^+ *m/z* 442–436, found *m/z* 442 (13), 441 (28), 440 (87), 439 (88), 438 (100), 437 (70), 436 (34), 331 (2), 330 (0.2), 329 (9), 328 (4), 327 (7), 326 (5), 325 (2), 129 (78), 110 (83). Anal. Calcd for $C_{14}H_{24}N_2Hg$: C, 39.95; H, 5.75; N, 6.65. Found: C, 39.74; H, 5.74; N, 6.73.

2,3-Bis(2,2-dimethylpropyl)butanedinitrile. Photolysis of **2** formed a 1:1 mixture of racemic and meso forms of the dimer isolated as a solid (mp 130–139 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 2.84–2.60 (m, 2 H), 1.96–1.80 (m, 2 H), 1.64–1.52 (two dd, 2 H), 1.04 (s, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 120.10/119.65, 43.98/43.77, 31.72/31.54, 30.73/30.67, 29.18 (broad). GC and HRMS: calcd for $C_{13}H_{22}N_2$ (M - 15^+) *m/z* 205.1705, found *m/z* 205.1701 (100), 149 (8), 110 (39), 95 (28), 57 (65). CIMS (NH_3): *m/z* 254 (M^+ + $2NH_3$, 30), 238 (M + NH_4^+, 100).

2-(2,2-Dimethylpropyl)pentanedinitrile. GCMS: *m/z* 165 (M + 1^+, 19), 149 (26), 108 (19), 96 (26), 81 (28), 57 (100).

2-(1,1-Dimethylethyl)-4,4-dimethylpentanenitrile. GCMS: *m/z* 168 (M + 1^+, 2), 152 (3), 110 (8), 96 (24), 57 (100).

2-(2,2-Dimethylpropyl)-4-pentenenitrile. Photolysis of CH_2=CHCN, *t*-BuHgCl (4 equiv), and CH_2=$CHCH_2Br$ (1 equiv) for 11 h formed the product in 49% yield in Me_2SO and 65% yield in PhH. ^1H NMR (300 MHz, $CDCl_3$): δ 5.89–5.75 (m, 1 H), 5.23–5.16 (m, 2 H), 2.60–2.52 (m, 1 H), 2.40–2.31 (m, 2 H), 1.69 (dd, *J* = 14.1, 10.5 Hz, 1 H), 1.38 (dd, *J* = 14.1, 2.7 Hz), 1.00 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.13, 122.99, 118.91, 45.59, 38.33, 30.69, 29.29, 26.86. GC and HRMS: calcd for $C_{10}H_{17}N$ *m/z* 151.1361, found *m/z* 151.1360 (1), 136 (4), 110 (6), 109 (9), 97 (4), 57 (100).

3,4,4-Trimethylpentanenitrile. Photolysis of *t*-BuHgI/KI with an *E*/*Z* mixture of crotononitrile in Me_2SO gave the reductive alkylation product. ^1H NMR (300 MHz, $CDCl_3$): δ 2.47 (dd, *J* = 16.8, 3.6 Hz, 1 H), 2.06 (dd, *J* = 16.8, 10.2 Hz, 1 H), 1.74–1.62 (m, 1 H), 1.07 (d, *J* = 6.9 Hz, 3 H), 0.90 (s, 9 H). GCMS: *m/z* 126 (M + 1^+, 0.7), 110 (18), 93 (2), 85 (6), 69 (39), 57 (100).

3,4,4-Trimethylpentanamide. Photolysis of *t*-BuHgI/KI with crotononitrile in the presence of PTSA·H_2O in Me_2SO found the amide isolated as a solid (mp 162–163 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 5.91 (br s, 1 H), 5.54 (br s, 1 H), 2.49–2.33 (m, 1 H), 1.85–1.73 (m, 2 H), 0.91 (d, *J* = 6.0 Hz, 3 H), 0.88 (s, 9 H). GC and HRMS: calcd for $C_{18}H_{17}NO$ *m/z* 143.1310, found *m/z* 143.1309 (14), 128 (17), 124 (5), 110 (6), 87 (61), 72 (71), 59 (100), 57 (91). FTIR (neat): ν = 3344, 3179, 1641 cm^{-1}.

2-Chloro-4,4-dimethylpentanenitrile.[17] ^1H NMR (300 MHz, $CDCl_3$): δ 4.44 (dd, *J* = 9.0, 5.4 Hz, 1 H), 2.70 (dd, *J* = 14.4, 9.0 Hz, 1 H), 1.98 (dd, *J* = 14.4, 5.4 Hz, 1 H), 1.05 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 118.1, 56.2, 39.3, 31.1, 29.3; GC and HRMS: *m/z* 148 (0.1), 146 (0.2), 130.0421 (M - 16^+, 8, calcd for C_6H_9ClN 130.0423), 94 (34), 89 (6), 67 (24), 57 (100).

(*E*)-2,3-Bis(2,2-dimethylpropyl)butenedinitrile. Mp: 103–104 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 2.53 (s, 4 H), 1.09 (s, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.0, 117.0, 47.5, 33.9, 33.9, 29.4. GC and HRMS: calcd for $C_{14}H_{22}N_2$ *m/z* 218.1783, found *m/z* 218.1782 (0.4), 162 (1), 147 (7), 105 (3), 57 (100). CIMS (isobutane): *m/z* 275 (M + 57^+, 100), 219 (M + 1^+, 31).

2,4,4-Trimethylpentanenitrile. Photolysis of methacrylonitrile (2 mmol), *t*-BuHgI (10 mmol), KI (10 mmol), and DABCO (5 mmol) in 10 mL of Me_2SO for 24 h formed 60% of the reductive *tert*-butylation product and 25% of the dimer of *t*-$BuCH_2C(CH_3)CN$. The mononitrile had ^1H NMR (300 MHz, $CDCl_3$): δ 2.65–2.53 (m, 1 H), 1.73 (dd, *J* = 14.1, 10.2 Hz, 1 H), 1.34 (d, *J* = 7.2 Hz, 3 H), 1.32 (dd, *J* = 14.1, 3.0 Hz, 1 H), 1.00 (s, 9 H). GCMS: *m/z* 126 (M + 1^+, 5), 110 (42), 83 (10), 69 (32), 57 (100). FTIR (neat): ν = 2235 cm^{-1}.

2,3-Dimethyl-2,3-bis(2,2-dimethylpropyl)butanedinitrile. The dimer was formed as a 1:1 mixture of diastereomers as judged by ^1H NMR. One diastereomer separated in pure form by column chromatography had mp 122–123 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 1.86 (d, *J* =

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14.1 Hz, 2 H), 1.59 (s, 6 H), 1.50 (d, J = 14.1 Hz, 2 H), 1.15 (s, 18 H). GC and HRMS: calcd for $C_{18}H_{28}N_2$ m/z 248.2253, found m/z 248.2255 (1), 191 (1), 177 (45), 125 (18), 110 (10), 94 (3), 68 (27), 57 (100). A mixture of the two diastereomers enriched in the second isomer had mp 75−85 °C and gave the following for the second isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.84 (d, J = 14.1 Hz, 2 H), 1.58 (s, 6 H), 1.53 (d, J = 14.1 Hz, 2 H), 1.16 (s, 18 H). The mass spectra of the two isomers were identical.

2-(2,2-Dimethylethyl)butanedinitrile (6).[17] The compound had mp 89−89.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.79−2.58 (m, 3 H), 1.12 (s, 9 H). GCMS: m/z 135 (M - 1$^+$, 0.1), 121 (21), 94 (28), 80 (8), 67 (17), 57 (100).

2-(2,2-Dimethylethyl)butenedinitrile (7). The compound was isolated as a solid (mp 119.0−119.5 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.91 (s, 1 H), 1.27 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.3, 114.2, 109.1, 108.9, 37.3, 27.9. GC and HRMS: calcd for $C_8H_{10}N_2$ m/z 134.0844, found m/z 134.0844 (3), 133.0767 (M − 1$^+$, 8, calcd for $C_8H_9N_2$ 137.0766), 119 (100), 107 (26), 107 (30), 92 (65), 76 (11), 65 (37), 57 (57).

(*E*)-2,3-Bis(2,2-dimethylethyl)butenedinitrile (8). The compound had mp 85−86 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.3, 115.9, 36.4, 29.6. GC and HRMS: calcd for $C_{12}H_{18}N_2$ m/z 190.1470, found m/z 190.1470 (1), 175 (5), 160 (3), 145 (1), 134 (10), 119 (3), 107 (2), 95 (11), 57 (100).

2,3-Bis(2,2-dimethylethyl)butanedinitrile (9). Two diastereomers were isolated, mp 83−85 and 175−176 °C. The low-melting isomer had the following ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.64 (s, 2 H), 1.26 (s, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 119.9, 41.6, 34.8, 27.6. GC and HRMS: calcd for $C_{12}H_{20}N_2$ m/z 192.1626, found m/z 192.1621 (0.06), 191.1547 (M - 1$^+$, 3, calcd for $C_{12}H_{19}N_2$ 191.1548), 177 (1), 161 (1), 135 (2), 121 (6), 94 (3), 82 (7), 69 (2), 57 (100). CIMS (isobutane): m/z 249 (M + 57$^+$, 100), 193 (M + 1$^+$, 48). The high-melting isomer had the following. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.57 (s, 2 H), 1.16 (s, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 118.3, 41.6, 34.3, 27.4. HRMS: calcd for $C_{12}H_{21}N_2$ (M + 1$^+$) m/z 193.1705, calcd for $C_{11}H_{17}N_2$ (M - 15$^+$) m/z 177.1393, found m/z 193.1710, 177.1391.

2,*N*-Bis(2,2-dimethylethyl)-3-cyano-4,4-dimethylpentanamide (10). The amide was isolated as two diastereomers, mp 168−173 and 212−216 °C. The lower melting isomer had the following. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.19 (br s, 1 H), 3.27 (d, J = 8.4 Hz, 1 H), 1.93 (d, J = 8.4 Hz, 1 H), 1.33 (s, 9 H), 1.20 (s, 9 H), 1.09 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 122.7, 54.8, 51.8, 41.7, 34.6, 33.9, 28.7, 28.4, 27.7. GC and HRMS calcd for $C_{16}H_{31}N_2O$ (M + 1$^+$) m/z 267.2436, found m/z 267.2441 (2), 251.2119 (M - 15$^+$, 2, calcd for $C_{15}H_{27}N_2O$ 251.2123), 209 (12), 195 (3), 184 (33), 166 (2), 153 (69), 128 (21), 110 (16), 97 (46), 57 (100). FTIR ($CDCl_3$): ν = 3373, 2233, 1672 cm^{-1}. The higher melting isomer had the following. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.59 (br s, 1 H), 2.53 (d, J = 1.8 Hz, 1 H), 2.14 (d, J = 1.8 Hz, 1 H), 1.37 (s, 9 H), 1.11 (s, 9 H), 1.09 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 120.9, 54.5, 51.7, 41.1, 34.4, 33.7, 28.4, 28.3, 28.0. GC and HRMS: calcd for $C_{16}H_{30}N_2O$ m/z 266.2358, found m/z 266.2352 (1), 251 (4), 210 (5), 194 (8), 184 (5), 166 (4), 153 (47), 128 (8), 110 (30), 97 (21), 57 (100). FTIR ($CDCl_3$): ν = 3373, 2233, 1672 cm^{-1}. Anal. Calcd for $C_{16}H_{30}N_2O$: C, 72.13; H, 11.35; N, 10.51. Found: C, 72.27; H, 11.08; N, 10.34.

(*E*)-2,3-Bis(1-methylethyl)butenedinitrile. The compound was isolated as a solid (mp 97−99 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.10 (sept, J = 6.6 Hz, 1 H), 1.22 (d, J = 6.6 Hz, 6 H). GC and HRMS: calcd for $C_{10}H_{14}N_2$ m/z 162.1157, found m/z 162.1154 (11), 147 (14), 132 (6), 120 (100), 93 (26), 82 (21), 43 (98).

***N*-Isopropyl Derivative of Isopropyl (1-Cyano-1-isopropyl-2-methylpropyl) Ketenimine (12).** Photolysis of 2,3-bis(1-methylethyl)-butenedinitrile with 10 equiv of *i*-PrHgCl, 20 equiv of KI, and 3 equiv of PTSA·H_2O for 48 h in Me_2SO gave 83% of the ketenimine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.64 (sept, J = 6.6 Hz, 1 H), 2.24 (sept, J = 6.6 Hz, 1 H), 2.03 (sept, J = 6.6 Hz, 1 H), 1.24 (d, J = 6.6 Hz, 6 H), 1.13 (d, J = 6.6 Hz, 12 H), 1.03 (d, J = 6.6 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.6, 120.9, 71.9, 55.3, 53.2, 34.3, 29.3, 23.8, 18.8, 17.8. GC and HRMS: calcd for $C_{16}H_{28}N_2$ m/z 248.2252, found m/z 248.2252 (3), 233 (2), 205 (7), 163 (100). Anal. Calcd for $C_{16}H_{28}N_2$: C, 77.36; H, 11.36; N, 11.28. Found: C, 77.38; H, 10.97; N, 11.45.

4-Cyano-2,2,5,5-tetramethyl-3-hexanone. Traces of the ketone were isolated from the photolysis of **7** with *t*-BuHgCl/KI/PTSA. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 1 H), 1.22 (s, 9 H), 1.16 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.0, 116.7, 46.4, 45.7, 35.2, 27.9, 26.1. GC and HRMS: calcd for $C_{11}H_{19}NO$ m/z 181.1467, found m/z 181.1464 (<1), 153 (0.5), 124 (0.4), 97 (3), 85 (11), 57 (100).

(2,2-Dimethyl-1-phenylpropyl)malononitrile (13a).[18] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (br s, 5 H), 4.22 (d, J = 5.7 Hz, 1 H), 3.00 (d, J = 5.7 Hz, 1 H), 1.08 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.2, 129.0, 128.4, 128.1, 113.3, 113.2, 56.3, 34.7, 28.2, 24.9. GC and HRMS: calcd for $C_{14}H_{16}N_2$ m/z 212.1314, found m/z 212.1315 (7), 197 (3), 156 (1), 132 (6), 105 (2), 91 (7), 77 (4), 57 (100).

(1,1,2,2-Tetramethylpropyl)malononitrile (13b). The product was isolated as a solid (mp 100−101 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.73 (s, 1 H), 1.25 (s, 6 H), 1.05 (s, 9 H). GC and HRMS: calcd for $C_{10}H_{15}N_2$ (M - 1) m/z 163.1235, found m/z 163.1236 (<1), 149.1078 (M - 15$^+$, calcd for $C_9H_{13}N_2$ 149.1079, 10), 122 (1), 108 (9), 99 (2), 83 (23), 69 (7), 57 (100).

[1-(1,1-Dimethylethyl)cyclohexyl]malononitrile (13c). Mp: 49−53 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.29 (s, 1 H), 1.92−1.22 (m, 10 H), 1.14 (s, 9 H). GC and HRMS: calcd for $C_{13}H_{19}N_2$ (M - 1) m/z 203.1548, found m/z 203.1551 (<1), 189.1395 (M - 15$^+$, 6, calcd for $C_{12}H_{17}N_2$ 189.1382), 121 (3), 81 (2), 67 (2), 57 (100).

Ethyl β-*tert*-Butyl-α-cyano-β-phenylpropionate (14). Photolysis of *t*-BuHgI (2 mmol), KI (2 mmol), and PTSA (2 mmol) with 0.5 mmol of ethyl (*E*)-α-cyanocinnamate in 10 mL of Me_2SO for 22 h gave 83% of the reductive alkylation product as a ~3:1 mixture of diastereomers which were not separated by GC or flash column chromatography. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42−7.16 (m), 4.05−3.90 (m), 3.85 (d, J = 9.0 Hz), 3.29 (d, J = 9.0 Hz), 3.14 (d, J = 5.1 Hz), 1.09 (s), 1.06 (s). GC and HRMS: calcd for $C_{16}H_{21}NO_2$ m/z 259.1572, found m/z 259.1573 (9), 244 (2), 203 (8), 186 (7), 176 (24), 130 (25), 91 (21), 77 (5), 57 (100).

α-*tert*-Butyl-*p*-phenylenedimalononitrile (15). The product (mp 113−117 °C) was eluted by ethyl acetate after impurities had been removed in flash column chromatography with hexane (93%)−ethyl acetate (7%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (qt, J = 8.4, 2.1 Hz, 4 H), 5.21 (br s, 1 H), 1.22 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.7, 129.4, 128.2, 127.6, 114.3, 111.2, 52.4, 41.8, 27.9, 25.5. GC and HRMS: m/z 262 (M$^+$, 0.4), 247.0987 (M - 15$^+$, 3, calcd for $C_{15}H_{11}N_4$ 247.0984), 182 (2), 141 (1), 77 (1), 57 (100); CIMS (isobutane): m/z 319 (M + 57$^+$, 100), 263 (M + 1$^+$, 46), 249 (84), 207 (8). CIMS (methane): m/z 263 (M + 1$^+$, 41), 207 (100).

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