Electron Transfer Chain Reactions in the Alkylation of Isonitriles by Alkylmercury Halides†
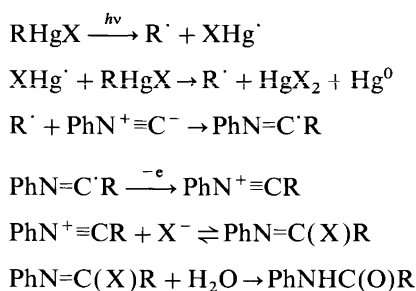
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Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday

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Imidoyl (PhN=CR˙) or acyl (RCO˙) radicals undergo electron transfer to alkylmercury halides in Me_2SO or PhH solution. Addition of t-Bu˙ or i-Pr˙ to isonitriles followed by electron transfer forms the nitrilium ion which is converted into the amide in Me_2SO, into the imidoyl halide in PhH, and into the amidine in PhH solution containing primary or secondary amines.

Isonitriles are known to be potent radicaphiles,[1–5] which yield imidoyl radicals (RN=C˙R′) that readily undergo β-elimination when R = alkyl.[1–3] Because of the ease of oxidation of imidoyl radicals to the nitrilium ion (RN⁺=CR′), we have investigated the participation of isonitriles in electron transfer chain (ETC) reactions involving secondary or tertiary alkylmercury halides (Scheme 1).

$$RHgX \xrightarrow{h\nu} R˙ + XHg˙$$

$$XHg˙ + RHgX \rightarrow R˙ + HgX_2 + Hg^0$$

$$R˙ + PhN^+\equiv C^- \rightarrow PhN=C˙R$$

$$PhN=C˙R \xrightarrow{-e} PhN^+\equiv CR$$

$$PhN^+\equiv CR + X^- \rightleftharpoons PhN=C(X)R$$

$$PhN=C(X)R + H_2O \rightarrow PhNHC(O)R$$

Scheme 1. (R = t-Bu or i-Pr).

Alkylmercury halides are mild oxidizing agents which are reduced to R˙, Hg^0 and X⁻ with a reduction potential of ≈ -0.6 V vs. SCE.[6,7] The rate of electron transfer to RHgCl from radical anions such as $RCMe_2NO_2˙^-$ or $PhC˙(O^-)CH_2R$ in Me_2SO increases with the stability of the incipient alkyl radical, suggesting that electron transfer to RHgX is dissociative with the stability of R˙ contributing to the transition state for electron transfer.[8]

Thus, secondary and tertiary alkylmercury halides are much more reactive than primary alkylmercury halides in ETC processes. Alkylmercury halides can also serve as initiators in free radical processes.[6] Convenient rates of initiation are observed at 25–35 °C upon fluorescent sunlamp irradiation in Me_2SO or PhH. In the presence of I⁻ in Me_2SO the photochemical initiation rate is increased and the formation of t-Bu˙ even becomes appreciable in the dark at 25 °C,[9] possibly because of comproportionation to form the thermally labile $(t$-Bu$)_2$Hg.[10] Because of the increased rate of initiation, the reactions of PhNC with t-BuHgCl were examined mainly in the presence of added iodide ion (KI in Me_2SO and Et_4NI in PhH).

Results

Photolysis of t-BuHgX or i-PrHgX with PhNC in Me_2SO at 35 °C leads to the precipitation of Hg^0 in a process inhibited by the presence of 10 mol% of $(t$-Bu$)_2NO˙$. The reaction also occurs in the dark at 80 °C with t-BuHgI and at 25 °C with the redox system KI–$K_2S_2O_8$. After work-up with aqueous $Na_2S_2O_3$ (to remove unchanged organomercurials), excellent yields of the amides PhNHC(O)R with R = t-Bu or i-Pr are found, Table 1. Reactions with primary alkylmercury halides were not investigated because results from other systems suggested they would be much less reactive than secondary or tertiary alkylmercurials.[8]
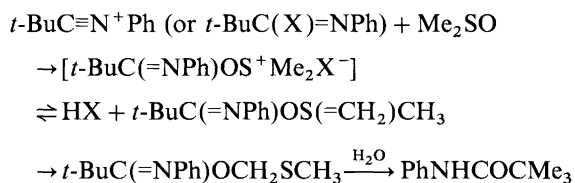
Scheme 1 predicts the initial formation of the imidoyl halide but GC–MS analysis of reaction mixtures in Me_2SO before aqueous work-up failed to detect this product. Instead this analysis revealed the formation of

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† Electron Transfer Processes. Part 62. For Part 61 see Russell, G. A., Wang, L. and Rajaratnam, R. *J. Org. Chem. 61* (1996) 8988.

Table 1. Reaction of *t*-BuHgX with PhNC to yield PhNHC(O)CMe$_3$ in Me$_2$SO.

t-BuHgX (X, equiv.)	KI (equiv.)	Conditions[a]	% PhNHC(=O)CMe$_3$[b]
Cl, 5	0	4 h, dark, 25 °C	0
Cl, 4	0	2 h, *hv*, 35 °C	42
Cl, 4	0	2 h, *hv*, 10 mol% (*t*-Bu)$_2$NO·, 35 °C	0
Cl, 4	0	4 h, *hv*, 35 °C	59
Cl, 4	0	4 h, 10 mol% (*t*-Bu)$_2$NO·, 35 °C	37
Cl, 4	4	4 h, *hv*, 35 °C	84
Cl, 4	4	4 h, HMPA, *hv*, 35 °C	76
Cl, 4	4	4 h, dark, 80 °C	54
Cl, 4	4	4 h, 2 equiv. K$_2$S$_2$O$_8$, dark, 25 °C	65

[a]0.5 Mmol of substrate in 10 ml of Me$_2$SO; *hv* = irradiation by a 275 W fluorescent sunlamp. [b]By GC or ^{1}H NMR with toluene as an internal standard.

t-BuC(=NPh)OCH$_2$SCH$_3$ in Me$_2$SO and the corresponding pentadeuterio compound in Me$_2$SO-*d$_6$*. Apparently the nitrilium ion, or the imidoyl halide, reacts readily with Me$_2$SO to form an intermediate that can undergo the Pummerer reaction,[11] Scheme 2.

t-BuC≡N$^+$Ph (or *t*-BuC(X)=NPh) + Me$_2$SO

→ [*t*-BuC(=NPh)OS$^+$Me$_2$X$^-$]

⇌ HX + *t*-BuC(=NPh)OS(=CH$_2$)CH$_3$

→ *t*-BuC(=NPh)OCH$_2$SCH$_3$ $\xrightarrow{\text{H}_2\text{O}}$ PhNHCOCMe$_3$

Scheme 2.

In the hope of observing the imidoyl halides the solvent was changed to PhH. Photolysis of *t*-BuHgCl with PhNC in PhH in the absence of I$^-$ afforded the imidoyl chloride which could be detected by GC–MS before hydrolysis or reduction to PhNHCH$_2$CMe$_3$ by NaBH$_4$ work-up.
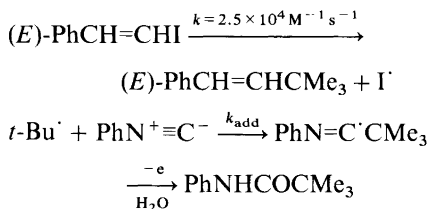
However, photolysis of PhNC and *t*-BuHgI or *t*-BuHgCl–KI for 4 h in PhH led to complex reaction mixtures in which the imidoyl halide could not be detected by GC–MS prior to work-up. With *t*-BuHgI, photolysis for 5 h produced **1** (30% yield) as the major product. With added primary or secondary amines (2 equiv.) in PhH the amidines **2** were formed in 85–90% yield. With 10 mol% of MeOH or EtOH the amide was again observed in high yield after hydrolysis, presumably formed by hydrolysis of the imino esters [ArN=C(OR)CMe$_3$]. In the absence of a nucleophilic trapping agent apparently the imidoyl iodide undergoes further ionic or homolytic reactions. One possible route to **1** is shown in Scheme 3 where unreacted *t*-BuHgX may serve as a Lewis acid catalyst.

PhN=C(I)CMe$_3$ ⇌ PhN$^+$≡CCMe$_3$ + I$^-$

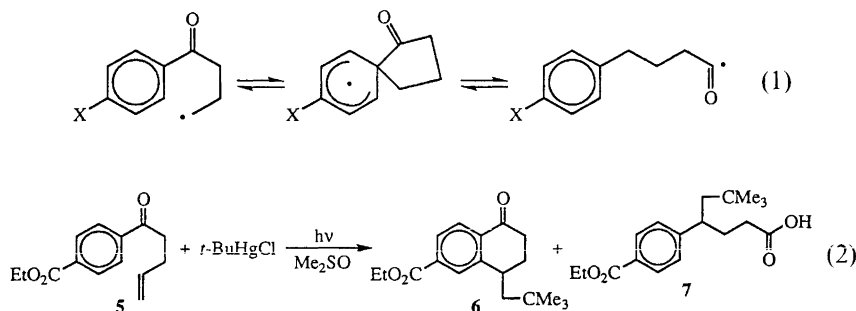PhN$^+$≡CCMe$_3$ + PhNC ⇌ PhN=C(CMe$_3$)C≡N$^+$Ph
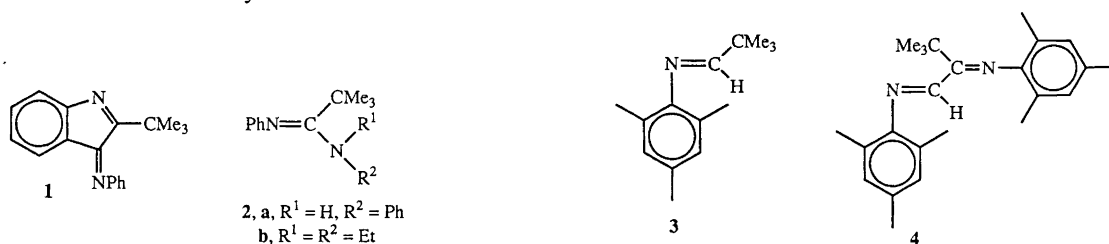
Scheme 3.

To avoid the cyclization to an indole derivative, the reaction of 2,4,6-trimethylphenyl isocyanide with *t*-BuHgX was examined. Photolysis in Me$_2$SO in the iodide promoted reaction gave the amide in 86% yield after hydrolytic work-up while in PhH with *t*-BuHgCl the imidoyl chloride could be detected by GC–MS before hydrolytic work-up. However, photolysis with *t*-BuHgI in PhH for 4 h failed to yield the imidoyl iodide by GC–MS. Instead the major products detected in addition to the amide (from traces of H$_2$O) were the imines **3** and **4**. Since this type of product was not observed with PhNC, and in Me$_2$SO excellent yields of the amide are formed, it appears that the imidoyl iodides are photochemically labile regenerating the imidoyl radical, which at low *t*-BuHgI concentrations can abstract benzylic hydrogen atoms from the mesityl groups. With PhNC in Me$_2$SO there was no evidence of this reaction occurring even in the presence of 2 equiv. of Ph$_3$CH. The formation of **4** is most reasonably formulated by addition of ArN$^+$≡CCMe$_3$ to ArNC as in Scheme 3. However with Ar = 2,4,6-trimethylphenyl cyclization cannot occur and a photochemically labile imidoyl iodide would be the initial reaction product.

1

2, a, R^1 = H, R^2 = Ph
   b, R^1 = R^2 = Et

3

4

The reactivity of t-Bu· towards PhNC in Me_2SO was measured by examining the competition of Scheme 4 at 35 °C.[12] From product analysis of the competitive photo-stimulated reaction of t-BuHgCl the reactivity of PhNC was measured to be 6.5-times that of (E)-PhCH=CHI, i.e., $k_{add} = 1.6 \times 10^5$ M^{-1} s^{-1}.

$$(E)\text{-PhCH=CHI} \xrightarrow{k = 2.5 \times 10^4 M^{-1} s^{-1}}$$

$$(E)\text{-PhCH=CHCMe}_3 + I\cdot$$

$$t\text{-Bu}^\cdot + \text{PhN}^+\!\!\equiv\!C^- \xrightarrow{k_{add}} \text{PhN=C}^\cdot\text{CMe}_3$$

$$\xrightarrow[H_2O]{-e} \text{PhNHCOCMe}_3$$

Scheme 4.

The initial kinetic chain length in the ETC reaction of t-BuHgCl with PhNC is appreciable with sunlamp initiation at 35 °C. Figure 1 shows the inhibition period created by 15 mol% of $(t\text{-Bu})_2NO^\cdot$ in a reaction monitored in $Me_2SO\text{-}d_6$ by ^1H NMR spectroscopy. The initial reactions rate is much greater (40–45) than the rate of radical production measured by the time required to consume the nitroxide, i.e., the initial kinetic chain length is 40–45. Shorter chain lengths are observed with higher rates of initiation, e.g., in the photostimulated reactions in the presence of I^-.

Fig. 1. Photostimulated reaction of t-BuHgCl with PhNC in $Me_2SO\text{-}d_6$ at 35 °C: ○, 0.133 M t-BuHgCl, 0.065 M PhNC; ●, in the presence of 0.020 M $(t\text{-Bu})_2NO^\cdot$.

containing Et_2NH the N,N-diethylamide of **7** was formed, reaction (2).

These results seem conclusively to demonstrate that acyl radicals can also undergo electron transfer to t-BuHgCl to form the acyl cation as the precursor to **7** or its amide, reaction (3). The oxidation of acyl radicals

Having established that electron transfer can occur from $ArN=C^\cdot R$ to t-BuHgX, we were interested in ascertaining whether a similar oxidation of acyl radicals could occur. Photolysis of t-BuHgCl or t-BuHgI in the presence of benzaldehyde produced little reaction other than the conversion of t-Bu· to isobutene and isobutane. Facile attack on aldehydic hydrogens is a process which occurs readily for electrophilic radicals (e.g., ROO·) rather than nucleophilic radicals such as t-Bu·. In fact, the preferred position of attack of t-Bu· on PhCHO is at the *para* position with $k \approx 1 \times 10^2$ M^{-1} s^{-1} but in the absence of a proton acceptor this addition is reversible.[13] In the presence of an amine, proton loss from the adduct radical followed by electron transfer to t-BuHgX occurs to yield 4-*tert*-butylbenzaldehyde by an ETC reaction.[13] Acyl radicals can also be formed by 1,4-phenyl migrations, e.g., reaction (1). Photolysis of t-BuHgCl with **5** in Me_2SO in the presence of DABCO gave a mixture of **6** (19%) and **7** (33%) after work-up, while in PhH

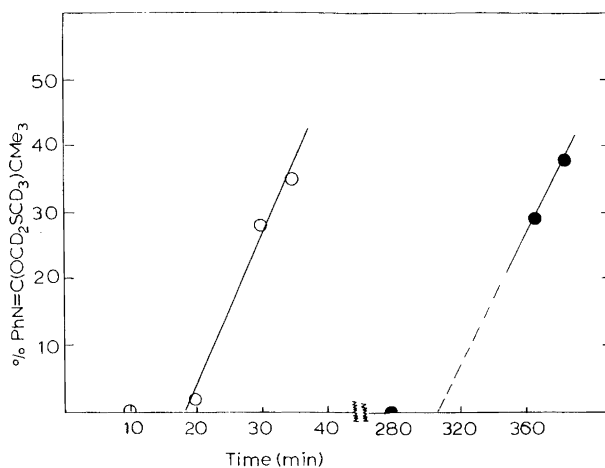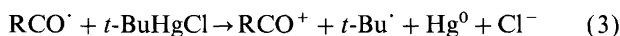by t-BuHgX must occur rapidly since there was no evidence of decarbonylation products.

$$\text{RCO}^\cdot + t\text{-BuHgCl} \rightarrow \text{RCO}^+ + t\text{-Bu}^\cdot + \text{Hg}^0 + \text{Cl}^- \qquad (3)$$

In conclusion, oxidative electron transfer to t-BuHgX has been demonstrated to occur for imidoyl and acyl radicals. Other easily oxidized neutral radicals which undergo electron transfer to t-BuHgX include amino-methyl radicals $(R_2NCH_2^\cdot)$,[14] and pyridinyl radicals,[7a,15] which are easily oxidized to the cations with E° values of ≈ -1 V (SCE).[7a,16–18] The $Bu_3Sn^\cdot$ radical, with an oxidation potential no lower than -0.43 V,[19] also reacts with alkylmercury halides to generate an alkyl radical,[20–22] probably by an electron transfer process.[22]

Experimental

General. ^1H and ^{13}C NMR spectra were obtained at 300 and 75 MHz for samples in $CDCl_3$ with Me_4Si as an

internal standard. Mass spectra were obtained with a Finnegan 4000 spectrometer in EI and CI modes and with high resolution with a Kratos MS-50 spectrometer. Most products were isolated by flash chromatography on silica gel (Kieselgel 60, 230–400 mesh ASTM) while thin layer separations used silica gel with hexane (90%)–ethyl acetate (10%) as the eluent. Photostimulated reactions utilized a Sylvania 275W sunlamp ≈20 cm from the reaction vessel which maintained a reaction temperature of 35 °C. tert-Butylmercury halides were prepared according to literature procedures.[12] Commercial Me_2SO was stored over molecular sieves and deoxygenated by nitrogen-bubbling before use.

Typical reactions were performed on a 0.5 mmol scale with work-up by aqueous $Na_2S_2O_3$ followed by CH_2Cl_2 extraction. For GC–MS analysis prior to work-up the reaction mixtures were passed through a Celite column and concentrated under vacuum.

Conversion of aryl isocyanides into N-*arylpropanamides.* Photolysis of PhNC with 4 equiv. of RHgCl and 4 equiv. of KI in Me_2SO for 4 h under nitrogen followed by work-up with aqueous $Na_2S_2O_3$, extraction with CH_2Cl_2 and evaporation of the solvent gave the N-phenyl-propanamide, which was isolated by column chromatography. 2,2-Dimethyl-N-phenylpropanamide had m.p. 128–129 °C (lit.[23] 127–128 °C) and a ^1H NMR spectrum in agreement with literature values.[23] HRMS: m/z 177.1154 (calc. for $C_{14}H_{15}NO$ 177.1154).

2-Methyl-N-phenylpropanamide was isolated as a white solid, m.p. 102–104 °C (lit.[21] 104–105 °C) with a ^1H NMR spectrum in agreement with the literature.[24] HRMS: m/z 163.0997 (calc. for $C_{16}H_{13}NO$ 163.0997).

2,2-Dimethyl-N-(2,4,6-trimethylphenyl)propanamide had ^1H NMR ($CDCl_3$): δ 1.34 (s, 9 H), 2.15 (s, 6 H), 2.26 (s, 3 H), 6.81 (s, 1 H), 6.87 (s, 2 H). GC–MS: m/z (relative intensity) 219 (M^+, 22), 62 (9), 135 (37), 134 (21), 120 (19), 119 (6), 91 (10), 57 (100).

Conversion of isonitriles into amidines. A mixture of the isonitrile, t-BuHgI (4 equiv.) and amine (2 equiv.) was stirred in PhH under N_2 for 4 h with sunlamp irradiation. Work-up with aqueous $Na_2S_2O_3$ and evaporation of the solvent gave the amidines, which were purified by column chromatography.

2,2-Dimethyl-N,N'-diphenylpropanamidine (**2a**) was isolated as a liquid from the reaction of PhNC, t-BuHgI and $PhNH_2$ benzene. ^1H NMR: ($CDCl_3$): δ 1.37 (s, 9 H), 6.60–6.80 (m, 5 H), 6.96 (m, 5 H). GC and HRMS: m/z (relative intensity) 252.1620 (7, calc. for $C_{17}H_{20}N_2$ 252.1627), 195 (4), 160 (54), 105 (8), 104 (100). FTIR ($CDCl_3$): 3427, 1641, 1498, 754, 692 cm^{-1}.

N,N-Diethyl-2,2-dimethyl-N^2-phenylpropanamidine (**2b**) was isolated as a liquid. ^1H NMR: δ 0.94 (t, $J=$ 6.9 Hz, 6 H), 1.32 (s, 9 H), 2.86 (q, $J=6.9$ Hz, 4 H), 6.72 (dd, $J=7.2$, 1.2 Hz, 2 H), 6.88 (t, $J=7.5$ Hz, 1 H), 7.20 (t, $J=7.5$ Hz, 2 H). GC and HRMS: m/z (relative intensity) 232.1935 (15, calc. for $C_{15}H_{24}N_2$: 232.1940),

203 (32), 175 (18), 160 (18), 147 (5), 119 (19), 105 (9), 104 (100). FTIR ($CDCl_3$): 1603, 1589, 1481, 763, 696 cm^{-1}.

Benzyl isocyanide with t-BuHgI and $PhNH_2$ yielded N^1-benzyl-2,2-dimethyl-N^2-phenylpropanamidine as a white solid, m.p. 62–63 °C. ^1H NMR: δ 1.25 (s, 9 H), 3.98 (s, 2 H), 4.56 (s, 1 H), 6.78 (d, $J=7.2$ Hz, 2 H), 6.84 (t, $J=7.5$ Hz, 1 H), 7.13–7.32 (m, 7 H). GC and HRMS: m/z (relative intensity) 266.1789 (10, calc. for $C_{18}H_{22}N_2$: 266.1783), 182 (8), 167 (5), 104 (11), 91 (100). FTIR ($CDCl_3$): 3449, 1649, 1591, 744, 696 cm^{-1}.

N^1-(1,1-Dimethylethyl)-2,2-dimethyl-N^2-phenylprop-anamidine was isolated as a liquid. ^1H NMR: δ 1.09 (s, 9 H), 1.36 (s, 9 H), 4.28 (s, 1 H), 6.65 (dd, $J=8.4$, 1.2 Hz, 2 H), 6.77 (tt, $J=7.2$, 1.2 Hz, 1 H), 7.14 (td, $J=8.1$, 0.6 Hz, 2 H). GC and HRMS: m/z (relative intensity) 232.1995 (26, calc. for $C_{15}H_{24}N_2$: 232.1940), 175 (14), 161 (3), 141 (6), 120 (8), 119 (100). FTIR ($CDCl_3$): 3583, 1736, 1647 cm^{-1}.

2-(1,1-Dimethylethyl)-3-phenylimino-3H-indole (**1**). Photolysis of 3 equiv. of t-BuHgI with PhNC in benzene gave **1** as a yellow solid, m.p. 100–101 °C. ^1H NMR: δ 1.54 (s, 9 H), 6.45 (d, $J=7.5$ Hz, 1 H), 6.83 (td, $J=8.4$, 0.9 Hz, 1 H), 6.92 (dd, $J=7.2$, 1.5 Hz, 2 H), 7.21–7.32 (m, 2 H), 7.39–7.44 (m, 3 H). ^{13}C NMR: δ 179.81 (s), 163.15 (s), 157.19 (s), 150.19 (s), 132.31 (d), 129.37 (d), 126.39 (d), 125.56 (d), 124.97 (d), 121.93 (s), 121.06 (d), 117.42 (d), 36.56 (s), 29.38 (q). GC and HRMS: m/z (relatively intensity) 262.1469 (86, calc. for $C_{18}H_{18}N_2$: 262.1470), 263 (14), 247 (20), 221 (26), 205 (8), 118 (23), 102 (9), 77 (100). FTIR ($CDCl_3$): 1643, 1608, 1593 cm^{-1}. Anal. Calc. for $C_{18}H_{18}N_2$: 82.40; H, 6.92; N, 10.60. Found: C, 82.07; H, 7.14; N, 10.44.

Trideuteriomethylthio)dideuteriomethyl 2,2-dimethyl-N-phenylpropanimidate [PhN=C(OCD_2SCD_3)CMe_3]. Photolysis of t-BuHgI in Me_2SO-d_6 for 3 h gave the imidate ester identified by GC–MS: m/z (relative intensity) 242 (M^+, 24), 207 (4), 194 (13), 193 (6), 192 (22), 185 (13), 160 (7), 157 (50), 57 (100). GC–MS (CI, isobutane) 243 (100).

2,2-Dimethyl-N-(2,4,6-trimethylphenyl)propanimidoyl chloride. Photolysis of t-BuHgCl with 2,4,6-trimethyl-phenyl isocyanide in PhH followed by filtration through Celite gave the imidoyl chloride detected by GC–MS: m/z (relative intensity) 237 (M^+, 13), 239 (4), 202 (42), 186 (3), 147 (11), 146 (100).

N-*(2,2-Dimethylpropylidene)-2,4,6-trimethylaniline* (**3**). ^1H NMR: δ 1.21 (s, 9 H), 2.03 (s, 6 H), 2.24 (s, 3 H), 6.82 (s, 2 H), 7.49 (s, 1 H). GC–MS: m/z (relative intensity) 203 (M^+, 27), 188 (10), 146 (100).

3,3-Dimethyl-1,2-bis(2,4,6-trimethylphenylimino)butane (**4**). GC–MS: m/z (relative intensity), 348 (M^+, 0.5), 334 (8), 333 (35), 281 (10), 208 (6), 207 (30), 202 (53), 144 (100). GC–MS (CI, ammonia): 349 (100).

Reaction of ethyl p-*(pent-4-enoyl)benzoate* (**5**) *with* t-*BuHgCl.* Photolysis of **5** with 3 equiv. of *t*-BuHgCl and 4 equiv. of DABCO in Me_2SO for 18 h produced **6** and **7** isolated by thin layer chromatography after work-up with aqueous $Na_2S_2O_3$ and CH_2Cl_2 extraction.

4-(2,2-Dimethylpropyl)-6-(ethoxycarbonyl)-α-tetralone (**6**). The ketone was isolated as a liquid. ^1H NMR: δ 1.06 (s, 9 H), 1.41 (t, $J = 7.2$ Hz, 3 H), 1.53 (dd, $J = 14.7$, 3.0 Hz, 1 H), 1.75 (dd, $J = 14.7$, 8.1 Hz, 1 H), 2.10–2.19 (m, 1 H), 2.27 (tt, $J = 13.5$, 4.5 Hz, 1 H), 2.62 (dt, $J = 17.7$, 4.8 Hz, 1 H), 2.85 (ddd, $J = 17.7$, 12.4, 5.1 Hz, 1 H), 3.13 (m, 1 H), 4.40 (q, $J = 7.2$ Hz, 2 H), 7.91 (dd, $J = 8.1$, 1.8 Hz, 1 H), 7.95 (s, 1 H), 8.04 (d, $J = 8.1$ Hz, 1 H). ^{13}C NMR: δ 198.03, 165.91, 150.24, 145.06, 134.58, 129.85, 127.19, 127.00, 61.37, 48.05, 34.70, 34.54, 31.45, 29.91, 28.13, 14.13. GC and HRMS: *m/z* (relative intensity) 288.1721 (35, calc. for $C_{18}H_{24}O_3$: 288.1725), 243 (14), 232 (14), 218 (74), 217 (100).

4-(4-Ethoxycarbonylphenyl)-6,6-dimethylheptanoic acid (**7**). The compound was isolated as a colorless liquid. ^1H NMR: δ 0.76 (s, 9 H), 1.38 (q, $J = 7.2$ Hz, 3 H), 1.56 (dd, $J = 14.1$, 3.3 Hz, 1 H), 1.72–2.18 (m, 1 H), 2.69–2.78 (m, 1 H), 4.36 (q, $J = 7.2$ Hz, 1 H), 7.22–7.25 (m, 2 H), 7.94–7.98 (m, 2 H), 10.5 (br s, 1 H). ^{13}C NMR: δ 178.97, 166.59, 151.75, 129.81, 128.52, 127.87, 60.81, 50.42, 41.95, 33.97, 31.92, 31.34, 30.03, 14.33. GC and HRMS: *m/z* (relative intensity) 306.1827 (48, calc. for $C_{18}H_{24}O_4$: 306.1831), 261 (28), 249 (65), 203 (64), 189 (92), 177 (100).

References

1. Shaw, D. H. and Pritchard, H. O. *Can. J. Chem. 45* (1967) 2749.
2. Saegusa, T., Kobayashi, S., Ito, Y. and Yasuda, N. *J. Am. Chem. Soc. 90* (1968) 4182.
3. Stork, G. and Sher, P. M. *J. Am. Chem. Soc. 105* (1983) 6765.
4. Barton, D. H. R., Ozbalik, N. and Bacher, B. *Tetrahedron 44* (1988) 3501.
5. Curran, D. P. and Liu, H. *J. Am. Chem. Soc. 113* (1991) 2127.
6. Russell, G. A. *Acc. Chem. Res. 22* (1989) 1.
7. (a) Kurosawa, H., Okada, H. and Hattori, T. *Tetrahedron Lett. 22* (1981) 4495; (b) Hush, N. S. and Oldham, K. B. *J. Electroanal. Chem. 6* (1963) 34.
8. Russell, G. A., Jiang, W., Hu, S. S. and Khanna, R. *J. Org. Chem. 51* (1986) 5498.
9. Russell, G. A., Hu, S., Herron, S., Baik, W., Ngoviwatchai, P., Wang, W., Nebgen, M. and Wu, Y.-W. *J. Phys. Org. Chem. 1* (1988) 299.
10. Blaukat, U. and Neuman, W. P. *J. Organomet. Chem. 49* (1973) 323.
11. Russell, G. A. and Mikol, G. J. In: Thyagarajan, B. S., Ed., *Mechanisms of Molecular Migrations,* Vol. 1, Wiley, New York 1968, p. 157.
12. Russell, G. A., Shi, B. Z., Kim, B. H., Jiang, W., Hu, S. and Baik, W. *J. Am. Chem. Soc. 117* (1995) 3952.
13. Russell, G. A., Kim, B. H. and Chen, P. *Unpublished results.*
14. Russell, G. A., Yao, C.-F., Rajaratnam, R. and Kim, B. H. *J. Am. Chem. Soc. 113* (1991) 373; Russell, G. A., Kulkarni, S. V. and Khanna, R. K. *J. Org. Chem. 55* (1990) 1080.
15. Russell, G. A., Rajaratnam, R., Wang, L., Shi, B. Z., Kim, B. H. and Yao, C.-F. *J. Am. Chem. Soc. 115* (1993) 10596.
16. Hawari, J. A., Kanabus-Kaminska, J. M., Wayner, D. D. M. and Griller, D. *Nato ASI Ser. C 184* (1986) 91.
17. Wayner, D. D. M., McPhee, D. J. and Griller, D. *J. Am. Chem. Soc. 110* (1988) 132.
18. Klippenstein, J., Arya, P. and Wayner, D. D. M. *J. Org. Chem. 56* (1991) 6736.
19. Tanner, D. D., Harrison, D. J., Chen, J., Kharrat, A., Wayner, D. D. M., Griller, D. and McPhee, D. J. *J. Org. Chem. 55* (1990) 3321.
20. Quirk, R. P. *J. Org. Chem. 37* (1972) 3554; Quirk, R. P. and Lea, R. E. *J. Am. Chem. Soc. 98* (1976) 5973.
21. Bloodworth, A. J. and Courtneidge, J. L. *J. Chem. Soc., Perkin Trans. 1* (1982) 1797.
22. Russell, G. A. and Ngoviwatchai, P. *Tetrahedron Lett. 26* (1985) 4975; Russell, G. A., Ngoviwatchai, P. and Tashtoush, H. I. *Organometallics 7* (1988) 696.
23. Mestres, R. and Palomo, C. *Synthesis* (1982) 288.
24. Fukawa, M., Hokama, N. and Okawara, T. *Synthesis* (1983) 42.