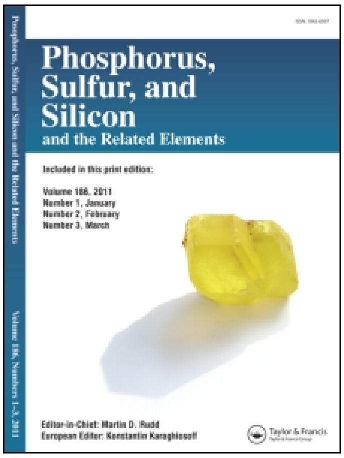

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THE REACTION OF DIPHENYL DISULFIDE WITH 3,3-DIACETYLPROPYL MERCURY CHLORIDE

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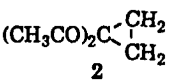
The enolate anion derived from $(CH_3CO)_2CHCH_2CH_2HgCl$ undergoes cyclization with demercuration to form 1,1-diacetylcyclopropane. The presence of Ph_2S_2 prevents cyclization and leads to phenylthylation at carbon and at mercury. In the absence of base Ph_2S_2 reacts with $(CH_3CO)_2CHCH_2CH_2HgCl$ in a photostimulated chain reaction to form $(CH_3CO)_2CHCH_2CH_2SPh$.

Key words: Diphenyl disulfide; mercury chloride; photostimulated reaction.

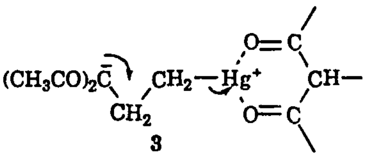
INTRODUCTION

The reaction of **1** with aqueous base has been reported to form Hg° and **2** via the transition state **3**.[1] Nucleophilic substitution at carbon in alkylmercurials by an S_N2 reaction is rare although there are now numerous examples of substitution occurring via the S_{RN} radical chain sequence.[2] We surmised that an intramolecular radical chain process might be involved in the conversion of **1** to **2** when it was observed that Ph_2S_2 completely prevented the formation of **2** in $Me_2SO/KOCMe_3$. However, Ph_2S_2 was not an inhibitor for a chain process but instead reacted with **3** and/or **1** to form **4** and **5**.

$(CH_3CO)_2CHCH_2CH_2HgCl$
1



2



3

$(MeCO)_2CHCH_2CH_2HgSPh$
4

$(MeCO)_2C(SPh)CH_2CH_2HgSPh$
5

$(MeCO)_2CHCH_2CH_2SPh$
6

RESULTS AND DISCUSSION

Photostimulated Reaction with Ph_2S_2

Compound **1** when irradiated by a fluorescent sunlamp with Ph_2S_2 in Me_2SO in the absence of base forms **4** and **6** (Table I). With 1 equiv. of Ph_2S_2 in 12 h, **6** is the major product (65–70%) accompanied by 5% of **4**. However, with 0.5 equiv. of Ph_2S_2, **4** and **6** are formed in about equal yields of 30 and 25%, respectively.

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TABLE I

Reactions of **1** in Me_2SO at 35–40°C

co-reactant (equiv.)	conditions[a]	product (% yield)[b]
Ph_2S_2 (1)	12 h, dark	no reaction
Ph_2S_2 (1)	12 h, hv	**6** (70), **4** (5)
Ph_2S_2 (1)	36 h, hv	**6** (66), **4** (trace)
Ph_2S_2 (0.5)	36 h, hv	**6** (30), **4** (25)
none	16 h, hv	no reaction
KI (4)	24 h, dark	**2** (5)
KI (4)	24 h, hv	**2** (26); $(MeCO)_2CHEt$ (22)
$KOCMe_3$ (1)	30 min, dark	**2** (61)
NaOMe	2 h, dark	**2** (58)
$Me_2C{=}NO_2Li$ (1)	2 h, dark or hv	**2** (47)
Ph_2S_2 (1), $KOCMe_3$ (1)	24 h, dark	**5** (35), **4** (23)
Ph_2S_2 (1), $KOCMe_3$ (1)	12 h, hv	**6** (22), **4** (15), **5** (9), $(MeCO)_2C(SPh)CH_2CH_2SPh$ (10)

[a] Reaction of 0.25 mmol of **1** in 5 ml of Me_2SO; hv = irradiation by a 275W sunlamp under N_2. [b] By GC and ^1H NMR integration with toluene as an internal standard.

Since no reaction occurs in the dark in the absence of base, reaction 1–3 must be occurring.

$$\mathbf{1} + Ph_2S_2 \xrightarrow{h\nu} \mathbf{6} + PhSHgCl \tag{1}$$

$$PhSHgCl + \mathbf{1} \rightarrow \mathbf{4} + HgCl_2 \tag{2}$$

$$\mathbf{4} + Ph_2S_2 \xrightarrow{h\nu} \mathbf{6} + Hg(SPh)_2 \tag{3}$$

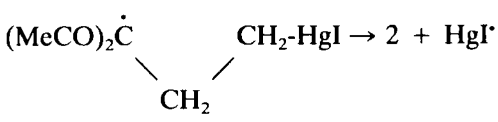
The photostimulated reaction is inhibited by $(t\text{-}Bu)_2NO^\bullet$ and from the observed inhibition periods an initial kinetic chain length of 30 was measured with 1 equiv. of Ph_2S_2. The conversion of **1** to **6** occurs via reactions 4 (X = Cl or SPh) and 5, as has been previously established for the reactions of numerous organomercury halides.[3,4] Diphenyl disulfide is readily attacked by free radicals (reaction 5) with a rate constant of 8×10^4 L/mol-s for 1°-alkyl radicals.[3]

$$PhS^\bullet + RHgX \rightarrow PhSHgX + R^\bullet \tag{4}$$

$$R^\bullet + PhSSPh \rightarrow RSPh + PhS^\bullet \tag{5}$$

Photochemical Decomposition of $(MeCO)_2CHCH_2CH_2HgX$

In Me_2SO photolysis of **1** occurs very slowly upon sunlamp irradiation or in a Rayonet photoreactor at 350 nm. In the presence of KI (4 equiv) the corresponding iodide, or mercurate complex,[5] photolyzed more readily and in 24 h with sunlamp irradiation formed $(MeCO)_2CHCH_2Me$ and **2** in ~ a 1:1 ratio although in relatively low yields of 22 and 26%, respectively. This suggests that in the absence of a radical trap, $(MeCO)_2CHCH_2CH_2^{\bullet}$ (formed by the photolysis of the mercurials) can abstract the methine hydrogen from **1** to yield a radical which can form **2** by S_Hi displacement of $HgI^{\bullet}$, reaction 6.



(6)

Reactions of $(MeCO)_2CHCH_2CH_2HgCl$ with Base

The formation of **2** and Hg° from **1** occurs readily in Me_2SO in the presence of $KOCMe_3$ (61% in 30 min) or NaOMe (58% in 2 h). Reaction was not observed with pyridine, DABCO or Li_2CO_3 in a 24 h reaction period. The reactions with $KOCMe_3$ or NaOMe are not photostimulated and $(t\text{-}Bu)_2NO^{\bullet}$ has no effect on the rate of formation of **2**. Compound **2** was also formed by reaction of **1** with $Me_2C{=}NO_2^-$ in the dark or upon irradiation. A radical trappable by $(t\text{-}Bu)_2NO^{\bullet}$ or $Me_2C{=}NO_2^-$ is not a precursor to **2** in cyclization promoted by bases. Apparently the S_Ni process described by **3** does indeed occur. However, upon addition of 1 equiv. of Ph_2S_2 in the dark, the reaction of **1** with $KOCMe_3$ produces as the only isolable products a mixture of **4** and **5** (Table I). The cyclopropane **2** is no longer detected. Some phenylthylating agent must trap **3** before the slow cyclization to **2** can occur. Diphenyl disulfide itself is not the agent since no reaction was observed in 24 h with the enolate anions formed from $(MeCO)_2CHCH_2Me$ or $(MeCO)_2CHCH_2CH_2SPh$ in Me_2SO. Under similar conditions **4** formed a trace (~5%) of **5** and **2** was again not detected.

One possible phenylthylating agent is a complex (**7**) of **1** or of $(MeCO)_2C(SPh)CH_2CH_2HgCl$ with Ph_2S_2. Upon reacting with enolate anions **7a**

$$\underset{\mathbf{7}}{RHgS(Ph)SPh^{+}Cl^{-}} + Nu:^{-} \rightarrow \mathbf{4} + \mathbf{5} + NuSPh \qquad (7)$$

$$\mathbf{7},\ \mathbf{a},\ R = (MeCO)_2CHCH_2CH_2$$
$$\mathbf{b},\ R = (MeCO)_2C(SPh)CH_2CH_2$$

would be converted to **4** and **7b** to **5**, reaction 7. At the same time the enolate anion derived from **1** would be converted to NuSPh = $(MeCO)_2C(SPh)CH_2CH_2HgCl$ (the precursor to **7b**), while the enolate anion derived from **4** would yield **5**. Compound **5** could also be formed in an intramolecular reaction from the enolate anion derived from **7a**. When the photolysis of **1** in the presence of both Ph_2S_2 and $KOCMe_3$ was performed, compounds **4**, **5** and **6** were formed accompanied by $(MeCO)_2C(SPh)CH_2CH_2SPh$, the phenylthylation product of the enolate anion derived from **6**. The enolate anions derived from **4** or **6** were also phenylthiolated by PhSCl (to yield **5** and $(MeCO)_2C(SPh)CH_2CH_2SPh$, respectively.

EXPERIMENTAL

3,3-Diacetylpropylmercury Chloride (**1**).[1] Material prepared according to the literature procedure had mp 132–133°C (lit.[1] 132.0–132.5); ^{1}H NMR ($CDCl_3$) δ 2.05 (t, 2H, *J* = 8.1 Hz), 2.187 (s, 6H), 2.666 (t, 2H, *J* = 8.1 Hz); GCMS *m/z* (relative intensity) 364 (M^+, 2), 336(14), 321(6), 127(100).

1,1-Diacetylcyclopropane (**2**).[1] The compound was isolated as a liquid bp 74°C; ^{1}H NMR ($CDCl_3$) δ 1.475 (s, 4H), 2.228 (s, 6H); GCMS *m/z* (relative intensity) 126 (M^+, 7), 111(23), 84(s), 69(36), 43(100); HRMS 126.0680 (calcd for $C_7H_{10}O_2$ 126.0681).

3-Ethyl-2,4-pentanedione.[6] The dione was isolated as a liquid by flash column chromatography (Kiesel gel 230–400 mesh ATSM) with hexane (99%)-ethyl acetate (1%) as the eluent. In $CDCl_3$ a 3:1 mixture of keto and enol forms was found by ^{1}H NMR integration. ^{1}H NMR (keto form) δ 0.905 (t, 3H, *J* = 7.5 Hz), 1.885 (m, 2H), 2.175 (s, 6H), 3.540 (t, 1H, *J* = 7.2 Hz); ^{1}H NMR (enol form) δ 1.047 (t, 3H, *J* = 7.5 Hz), 2.257 (q, 2H, *J* = 7.5 Hz), 2.139 (s, 6H); GCMS of mixture *m/z* (relative intensity 128 (M^+, 2), 113(2), 100(7), 86(30), 85(5), 71(59), 58(5), 55(2), 44(3), 43(100).

3,3-Diacetylpropylmercury Phenyl Sulfide, **4**. The compound was isolated by flash chromatography. In $CDCl_3$ solution a 3:1 mixture of keto and enol and forms was indicated by ^{1}H NMR integration. ^{1}H NMR (keto form) δ 1.552 (t, 2H, *J* = 8.4 Hz), 2.130 (s, 6H), 2.280 (m, 2H), 3.558 (t, 1H, *J* = 6.9 Hz), 7.150–7.230 (m, 3H), 7.360–7.420 (m, 2H); ^{13}C NMR (keto form) δ 27.17(t), 29.29(q), 32.93(t), 72.16(d), 125.32(d), 128.75(d), 132.98(d), 135.32(s), 204.00(s); ^{1}H NMR (enol form) δ 1.806 (t, 2H, *J* = 6.9 Hz), 2.101 (s, 6H), 2.632 (t, 2H, *J* = 8.1 Hz), 7.070–7.140 (m, 3H), 7.360–7.420 (m, 2H); ^{13}C NMR (enol form) δ 22.87(q), 26.56(t), 36.16(t), 113.88(s), 125.32(d), 128.75(d), 132.98(d), 135.32(s), 190.80(s); GC and HRMS *m/z* (relative intensity) 438.0589 (M^+, 0.4, calcd. for $C_{13}H_{16}O_2SHg$ 438.0577), 420(2), 218(9), 185(3), 154(5), 127(26), 110(27), 109(88), 85(21), 77(7), 69(15), 65(38), 51(9), 43(100).

3,3-Diacetyl-3-(phenylthiyl)propylmercury Phenyl Sulfide, **5**. The compound was isolated as a solid, mp 101–102°C, by flash column chromatography; ^{1}H NMR ($CDCl_3$) δ 1.387 (t, 2H, *J* = 7.2 Hz), 2.281 (s, 6H), 2.457 (t, 2H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 26.48(q), 27.42(t), 29.87(t), 86.39(s), 125.49(d), 129.29(d), 129.78(d), 133.18(d), 135.18(d), 135.88(s), 200.99(s); GC and HRMS *m/z* (relative intensity) 546.0604 (M^+, 0.7, calcd. for $C_{19}H_{20}O_2S_2Hg$ 546.0611), 274(4), 235(4), 218(7), 207(10), 193(25), 192(28), 175(12), 165(6), 123(16), 110(26), 109(100). Anal. Calcd. for $C_{19}H_{20}O_2S_2H_6$: C, 41.87; H, 3.70; S, 11.76. Found: C, 41.97; H, 3.72; S, 11.82.

3,3-Diacetylpropyl Phenyl Sulfide, **6**. The compound was isolated as a liquid by flash column chromatography. In $CDCl_3$ a 2:1 ratio of keto and enol forms was found by ^{1}H NMR integration. ^{1}H NMR (keto form) 2.060–2.170 (m, 2H), 2.145 (s, 6H), 2.883 (t, 2H, *J* = 7.2 Hz), 3.917 (t, 1H, *J* = 6.9 Hz), 7.160–7.400 (m, 5H); ^{13}C NMR (keto form) δ 27.16(t), 29.31(q), 31.58(t), 66.46(d), 126.38(d), 128.98(d), 129.54(d), 135.14(s), 203.48(s); ^{1}H NMR of enol form δ 2.059 (s, 6H), 2.522 (t, 2H, *J* = 8.2 Hz), 2.906 (t, 2H, *J* = 9.0 Hz), 7.160–7.140 (m, 5H); ^{13}C NMR (enol form) δ 22.85(q), 27.80(t), 34.25(t), 108.69(s), 126.53(d), 128.92(d), 130.06(d), 135.55(s), 191.28(s); FTIR 3408, 3061, 2922, 1724, 1699, 1358 cm^{-1}; GC and HRMS *m/z* (relative intensity) 236.0875 (M^+, 5, calcd for $C_{13}H_{16}O_2S$ 236.0871), 137(7), 136(62), 135(23), 127(12), 123(7), 113(16), 91(5), 85(17), 45(15), 43(100). Anal. calcd for $C_{13}H_{16}O_2S$: C, 66.06; H, 6.82; S, 13.58. Found: C, 65.91; H, 6.78; S, 14.44.

3,3-Diacetyl-3-(phenylthiyl)propyl Phenyl Sulfide. The compound was isolated as a liquid by flash column chromatography; ^{1}H NMR ($CDCl_3$) δ 2.135 (t, 2H, *J* = 8.1 Hz), 2.276 (s, 6H), 2.884 (t, 2H, *J* = 8.1 Hz), 7.170–7.390 (m, 10H); GCMS *m/z* (relative intensity) 344 (M^+, 4), 302(6), 235(3), 208(5), 166(16), 149(27), 123(88), 109(10), 91(8), 77(13), 65(10), 45(62), 41(100).

Determination of Product Yields. Reaction products obtained in deoxygenated Me_2SO were added to water and extracted with Et_2O or CH_2Cl_2. The dried extracts ($MgSO_4$) were concentrated under vacuum and a known amount of toluene added as an internal standard for ^{1}H NMR integration in $CDCl_3$ with qualitative verification of products by GC. Photochemical reactions were performed in pyrex tubes under N_2 with irradiation by a 275W fluorescent sunlamp. The kinetic chain length for the photostimulated reaction of **1** with Ph_2S_2 was followed by ^{1}H NMR in a 6 mm NMR tube. Tubes containing 0.1 mmol each of **1**, Ph_2S_2 and $PhCH_3$ in 1 ml of $Me_2SO\text{-}d_6$ were irradiated under identical conditions with a 275W fluorescent sunlamp. In the absence of $(t\text{-Bu})_2NO^\bullet$ an initial rate of formation of **6** of 0.00225 mol/L-min was observed. In the presence of 0.01 mol of $(t\text{-Bu})_2NO^\bullet$ no reaction was observed for 150 min after which a rate of ~0.00225 mol/L-min was observed. The rate of initiation under the reaction conditions was thus 0.00007 mol/L-min. The rate of the photostimulated reaction in the presence of 0.2 mmol of KI was further accelerated by a factor of ~2.

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