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Reaction of Sterically Crowded Selenoketones with Propiolic Acid

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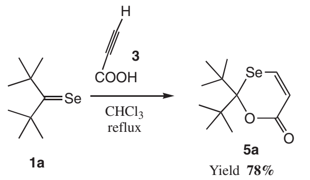
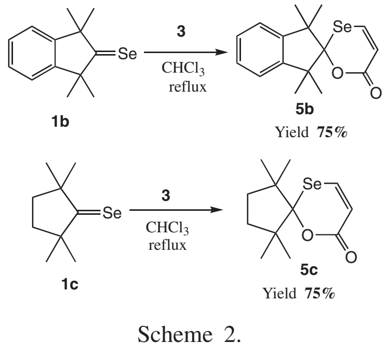
The reaction of di-*t*-butyl selenoketone with propiolic acid gave 2*H*,6*H*-1,3-oxaselenin-6-one in 78% yield, whereas the reaction of di-*t*-butyl thioketone with propiolic acid recovered the starting thioketone almost quantitatively.

It is well known that α,β-unsaturated thiones reacted with acetylenes to afford the corresponding [4 + 2] cycloadducts.[1] The reaction of selenocarbonyl compounds (**1**) is of current interest.[2] Recently, we have found that isolable thioketones (**2**) reacted with propiolic acid (**3**) to give 2*H*,6*H*-1,3-oxathiin-6-ones (**4**).[3] These results prompted us to investigate the reaction of selenoketones **1** with **3**. In this paper, we report on the first isolation of 2*H*,6*H*-1,3-oxaselenin-6-ones (**5**).

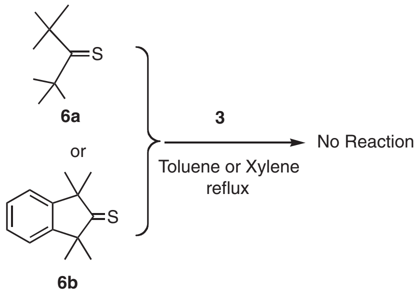
We first tried the reaction of di-*t*-butyl selenoketone (**1a**) with **3**. The treatment of selenoketone **1a** with **3** resulted in the formation of 2,2-di-*t*-butyl-2*H*,6*H*-1,3-oxaselenin-6-one (**5a**) in 78% yield (Scheme 1). 1,1,3,3-Tetramethylindan-2-selone (**1b**) and 2,2,5,5-tetramethylcyclopentane-1-selone (**1c**) also reacted with **3** to give the corresponding 2*H*,6*H*-1,3-oxaselenin-6-ones (**5b**,**c**) in good yields (Scheme 2).



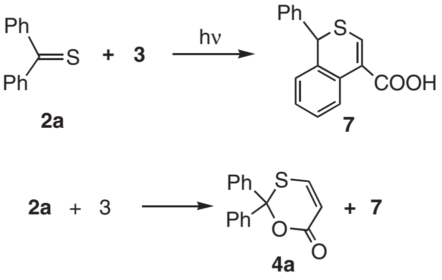
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

We then tried the reaction of sterically crowded thioketones (**6**), such as di-*t*-butyl thioketone (**6a**) and 1,1,3,3-tetramethylindan-2-thione (**6b**), with **3** to compare the reactivity with selones. The treatment of **6a** with **3** in refluxing toluene resulted in the recovery of **6a** almost quantitatively. The reaction of **6b** with **3** gave the same result. An attempted synthesis of 2*H*,6*H*-1,3-oxathiin-6-ones failed, even in refluxing xylene (Scheme 3).

In 1970, Ohno et al. described the photocycloaddition of thiobenzophenone (**2a**) with **3**, which furnished 1-phenyl-1*H*-isothiochromene-4-carboxylic acid (**7a**). The authors assumed that the addition of the π,π^* triplet state of **2a** to the acetylenic bond proceeded, and was followed by intramolecular hydrogen migration.[4] Gotthardt and Nierberl discovered the cycloaddition of **2a** with propiolic acid and its ester.[5] 4,4′-Dimethoxyselenobenzophenone has been known to react with propiolic acid to give 6-oxo-1-(4-methoxyphenyl)-6*H*-isoselenochromene-4-carboxylic acid.[6] To investigate the difference in the reactivity between selenobenzophenone and thiobenzophenone, we then tried the reaction of **2a** with **3**. The treatment of thione **2a** with **3** in refluxing toluene resulted in the formation of 2,2-diphenyl-2*H*,6*H*-1,3-oxathiin-6-one (**4a**) and **7a** in 35 and 32% yields, respectively (Scheme 4). Selenobenzophenone is more reactive toward **3** than thiobenzophenone, which results in the exclusive formation of an isoselenochromene derivative via a less-hindered transition state. The present reaction is the first example of the formation of thiodioxenone (**4**) from thiobenzophenone.

We then tried the reaction of 4′-methoxyselenopivalophenone (**1d**), which has one aromatic group next to selenocarbonyl, with **3**. Since diselenetane (**8**) undergoes thermal cycloreversion to give **1d**, the reaction was carried out in refluxing toluene.[7] The obtained products were selenodioxenone (**5d**) and 4′-methoxypivalophenone in 25 and 15% yields, respectively (Scheme 5). Starting **7** was recovered in 42%. Trace amount of 1-(4′-methoxyphenyl)-6-methoxy-1*H*-isoselenochromene-

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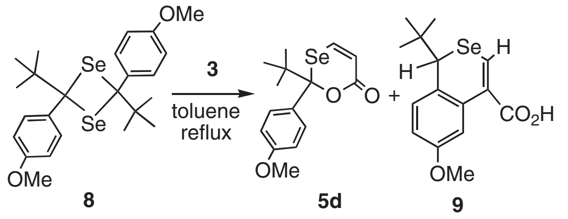

Scheme 5.

4-carboxylic acid (**9**) was formed, whereas analytically pure sample was not obtained. Due to the low reactivity of **1d** toward **3**, **1d** is easily oxidized to give 4′-methoxypivalophenone. In contrast to 4,4′-dimethoxyselenobenzophenone, 4′-methoxyselenopivalophenone gave two types of different products. The lower yields might be due to the tendency of the dimerization of **1d**.

Experimental

General. Flash chromatography was carried out by Merck Kieselgel 60 (230–400 mesh). NMR spectra were measured on a Varian Innova-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C). The melting points were uncorrected.

Materials. Selenoketones, **1a**–**c** were prepared by the method described by Okazaki and Guziec et al.[8]

Reaction of Di-*t*-butyl Selenoketone with Propiolic Acid. To a refluxing solution of selenoketone **1a** (205 mg, 1.0 mmol) in chloroform (10 mL) was added **3** (210 mg, 3.0 mmol) in chloroform (5 mL). After refluxing for 5 h, the reaction mixture was evaporated to afford a pale-yellow oil, which was chromatographed over silica gel by elution from hexane–dichloromethane (1:1) to give 2,2-di-*t*-butyl-2*H*,6*H*-1,3-oxaselenin-6-one (**5a**) (214 mg, 0.78 mmol). Compound **5a**: Colorless crystals, mp 95–96 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.28 (s, 18H, *t*-Bu), 6.28 (d, 1H, $J = 10$ Hz, =CH), 7.79 (d, 1H, $J = 10$ Hz, =CH). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 28.62 (*t*-Bu), 46.40 (q-C), 109.15 (Se–C–O), 114.32 (=C), 141.85 (=C), 161.68 (C=O). Anal. Found: C, 52.00; H, 7.19%. Calcd for $C_{12}H_{20}O_2Se$: C, 52.36; H, 7.32%.

Other reactions were carried out in a similar manner.

1,1,3,3-Tetramethylindan-2-selone-Adduct (5b): Colorless crystals, mp 169–170 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.39 (s, 6H, CH$_3$), 1.53 (s, 6H, CH$_3$), 6.28 (d, 1H, $J = 11$ Hz, =CH), 7.12–7.21 (m, 4H, Ar), 7.71 (d, 1H, $J = 11$ Hz, =CH). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 24.71 (CH$_3$), 30.43 (CH$_3$), 54.01 (q C), 106.36 (Se–C–O), 116.91 (=CH), 122.25 (Ar), 127.55 (Ar), 138.70 (=CH), 146.02 (Ar), 162.61 (COO). Anal. Found: C, 60.19; H, 5.65%. Calcd for $C_{16}H_{18}O_2Se$: C, 59.82; H, 5.65%.

2,2,5,5-Tetramethylselenocyclopentanone-Adduct (5c): Colorless crystals, mp 112–113 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.18 (s, 6H, CH$_3$), 1.23 (s, 6H, CH$_3$), 1.61 (q, 2H, CH$_2$), 1.88 (q, 2H, CH$_2$), 6.27–6.30 (d, 2H, $J = 10$ Hz, =CH), 7.72–7.74 (d, 2H, $J = 10$ Hz). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 27.59 (CH$_3$), 29.05 (CH$_3$), 38.18 (CH$_2$), 50.71 (q-C), 106.90 (Se–C–O), 117.26 (=CH), 139.03 (=CH), 163.61 (COO). Anal. Found: C, 53.00; H, 6.61%. Calcd for $C_{12}H_{18}O_2Se$: C, 52.75; H, 6.64%.

Reaction of 2a with 3. To a refluxing solution of thiobenzophenone **2a** (226 mg, 1.0 mmol) in toluene (10 mL) was added **3** (154 mg, 2.2 mmol) in toluene (5 mL). After refluxing for 10 h, the reaction mixture was evaporated to afford a brown oil, which was chromatographed over silica gel by elution from hexane–dichloromethane (1:1) and then dichloromethane to give 2,2-diphenyl-2*H*,6*H*-1,3-oxathiin-6-one (**4a**) (104 mg, 0.35 mmol) and **7** (94 mg, 0.32 mmol). Compound **4a**: Colorless crystals, mp 126–127 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.18 (s, 6H, CH$_3$), 6.09 (d, 1H, $J = 10.4$ Hz, =CH), 7.28–7.40 (m, 7H, Ar and =CH), 7.55–7.60 (m, 4H, Ar). Anal. Found: C, 71.73; H, 4.57%. Calcd for $C_{16}H_{12}O_2S$: C, 71.62; H, 4.51%. Compound **7**: mp 189–190 °C (lit.[4] mp 189–190 °C).

Reaction of 2,4-Di-*t*-butyl-2,4-bis(*p*-methylphenyl)-1,3-diselenetane, 8 with 3. To a refluxing solution of diselenetane **8** (242 mg, 0.5 mmol) in toluene (10 mL) was added propiolic acid (154 mg, 2.2 mmol) in toluene (5 mL). After refluxing for 25 h, the reaction mixture was evaporated to afford a dark-brown oil, which was chromatographed over silica gel by elution from hexane–dichloromethane (1:1) to give 2-*t*-butyl-2-*p*-methylphenyl-2*H*,6*H*-1,3-oxaselenan-6-one (**5d**) (81 mg, 0.25 mmol) and **9** (3 mg, 0.01 mmol). Compound **5d**: Colorless crystals, mp 122–124 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.10 (s, 9H, CH$_3$), 3.79 (s, 3H, OMe), 6.21 (d, 1H, $J = 10.4$ Hz, =CH), 6.78 (d, 2H, $J = 8.8$ Hz, Ar), 7.50 (br d, $J = 8.8$ Hz, Ar), 7.70 (d, 1H, $J = 10.4$ Hz, =CH). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 27.20 (CH$_3$), 41.69 (q-C), 55.61 (OMe), 103.30 (Se–C–O), 112.39 (Ar), 117.94 (=CH), 130.33 (Ar), 131.11 (Ar), 140.33 (=CH), 159.75 (Ar), 164.17 (COO). Anal. Found: C, 55.41; H, 5.59%. Calcd for $C_{15}H_{18}O_3Se$: C, 55.39; H, 5.58%. Purification of compound **9** was failed due to its poor yield. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.93 (s, 9H, CH$_3$), 3.78 (br s, 1H, CH), 3.82 (s, 3H, OMe), 6.86 (dd, 1H, $J = 2.4$ and 8.8 Hz, Ar), 7.04 (d, 1H, $J = 8.8$ Hz, Ar), 7.43 (d, 1H, $J = 2.4$ Hz, Ar), 8.43 (s, 1H, =CH).

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