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Synthesis and Hydrolysis of *p*-Toluoyl and Acetyl 9-Triptycyl Diselenides: A Study on Generation of Triptycene-9-selenenoselenoic Acid

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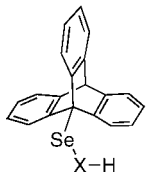
ABSTRACT: *p-Toluoyl 9-triptycyl diselenide (**9**) was prepared by reaction of Se-9-triptycyl triptycene-9-selenoseleninate (**7**) with p-toluenecarboselenoic acid (**8**) and by reaction of triptycene-9-selenenoselenolate salt with p-toluoyl chloride. Acetyl 9-triptycyl diselenide (**13**) was prepared by reaction of triptycene-9-selenenoselenolate salt with acetyl chloride. Hydrolysis of the two diselenides, **9** and **13**, provided triptycene-9-selenol (**10**) and di-9-triptycyl triselenide (**12**), suggesting the generation of triptycene-9-selenenoselenoic acid (**3**).* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:525–528, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20155

INTRODUCTION

Selenenoselenoic acid (R-Se-Se-H) is a chalcogenenochalcogenoic acid (R-X-Y-H; X, Y = O, S, Se, Te) and a homolog of selenenic (R-Se-O-H) and selenenothioic acids (R-Se-S-H). While selenenic acids have been drawing considerable attention for decades [1,2], the chemistry of selenenothioic acids and selenenoselenoic acids has been scarcely explored. To our knowledge, there had been only a few reports on selenenothioic acids and the salts, which are based on observation of $H_2NCH_2CH_2SeSH$ by UV-vis spectroscopy [3] and of RSeSLi (R = Bu, Ph) in THF by ^{77}Se NMR spectroscopy [4], until our report on the isolation of triptycene-9-selenenothioic acid (**2**) [5]. MeSeSH was taken up in a recent computational study [6]. Selenenoselenoic acids were unknown up to now, and only the lithium salts in solution have been reported [4].

R-X-Y-H
Chalcogenenochalcogenoic Acids
X, Y = O, S, Se, Te



X = O (**1**), S (**2**), Se (**3**)
(Trip-Se-XH)

We have also reported the synthesis of triptycene-9-selenenic acid (**1**) [7]. Acids **1** and **2** are stabilized by a sterically demanding 9-triptycyl group [8] (abbreviated as Trip hereafter) from the dimerization accompanying elimination of H_2O and H_2S, respectively. As the precursor for selenenoselenoic acids, their acyl or aroyl derivatives, $RSeSeC(O)R'$, are promising candidates, on the analogy of the syntheses of sulfenothioic acids

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(R-S-S-H) [9] and selenenothioic acid **2**. Aroyl aryl diselenides [ArC(O)SeSeAr′ **4**] have been synthesized by reactions of potassium arenecarboselenoates [10] or *Se*-tin [11] or *Se*-germanium [12] arenecarboselenoates with areneselenenyl bromides (Eq. (1)). We report here the synthesis of TripSeSeC(O)R (R = *p*-Tol and Me) by alternative reactions and their hydrolysis suggesting the generation of TripSeSeH (**3**).

$$\underset{\text{M = K, Ar''}_3\text{Sn, Ar''}_3\text{Ge}}{\text{ArC(O)SeM + Ar'SeBr}} \longrightarrow \underset{\textbf{4}}{\text{ArC(O)SeSeAr'}} \qquad (1)$$

RESULTS AND DISCUSSION

Acetyl disulfides **5** [13] and acetyl selenenothioate **6** [5] were previously prepared by the reaction of thiosulfinates [RS(O)SR] and selenoseleninates [RSe(O)SeR], respectively, with thioacetic acid (Eq. (2)). In a similar manner, *Se*-9-triptycyl triptycene-9-selenoseleninate (**7**) [7] was treated with 2 molar amounts of *p*-toluenecarboselenoic *Se*-acid (**8**) to give the desired *p*-toluoyl 9-triptycyl diselenide (**9**) in high yield (Eq. (3)). *Se*-Acid **8** was prepared in situ by acidification of the corresponding sodium salt [14] with HCl gas in acetone.

$$\underset{\text{X = S, Se}}{\text{RX(O)XR}} \xrightarrow{\text{2AcSH}} \underset{\textbf{5}\text{: X = S}\quad \textbf{6}\text{: X = Se}}{\text{2 RXSAc}} \qquad (2)$$

$$\underset{\textbf{7}}{\text{Trip-Se(O)-Se-Trip}} + \underset{\text{(2 molar equiv)}\quad \textbf{8}}{\text{HSeC(O)-}p\text{-Tol}} \xrightarrow[0\ ^\circ\text{C, 1 h}]{\text{CH}_2\text{Cl}_2} \underset{\textbf{9}\ 83\%}{\text{Trip-Se-Se-C(O)-}p\text{-Tol}} \qquad (3)$$

The reaction of a selenenoselenolate salt (R-Se-Se$^-$) [4] with acid chloride is more straightforward for the synthesis of diselenide **4**. Thus, triptycene-9-selenol (**10**) was deprotonated with *t*-butyllithium in THF at 0°C, and the resulting selenolate salt **11** was allowed to react with elemental selenium, followed by treatment with *p*-toluoyl chloride to give **9** in 24% yield together with triselenide **12** (54%). In a similar manner, acetyl derivative **13** was prepared in 25% yield. When a mixture containing TripSeSe$^-$ (the deprotonation was carried out with NaH) was quenched with hydrochloric acid, selenol **10** and triselenide **12** were formed in a ratio of 53:47 (see Scheme 1), and selenenoselenoic acid **3** was not obtained. Incidentally, when elemental sulfur was used instead of elemental selenium, the ^{1}H NMR spectrum of the mixture showed the formation of TripSeSH (**2**) [5], (TripSe)$_2$S [5], (TripSe)$_2$, and TripH in a ratio of 11:62:8:19.

$$\underset{\textbf{10}}{\text{TripSeH}} \xrightarrow[\text{THF, 0 °C}]{t\text{-BuLi}} \underset{\textbf{11}}{\text{TripSeLi}}$$

$$\xrightarrow[\text{2. RCOCl}]{\text{1. Se}} \underset{\textbf{9}\text{: R = }p\text{-Tol (24\%)}\quad \textbf{13}\text{: R = Me (25\%)}}{\text{TripSeSeC(O)R}} + \underset{\textbf{12}}{\text{(TripSe)}_2\text{Se}}$$

SCHEME 1

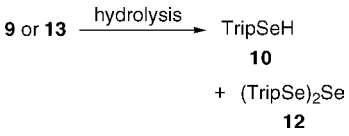
Hydrolysis of **9** and **13** was investigated. Hydrolysis of **9** with 60% perchloric acid in refluxing ethanol gave a mixture of selenol **10** and triselenide **12** (Eq. (4)). The ratio of the two products was dependent on the starting concentration of **9**. Thus, in the case of high concentration of **9** (1.0×10^{-2} M), **10** and **12** were formed in a ratio of 44:56 (Table 1, run 1), and in lower concentration (1.8×10^{-3} M), **10** and **12** were formed with recovery of **9** in a ratio of 82:10:8 (run 2). The hydrolysis at lower temperature did not affect the result (**10**/**12** = 81/19) (run 3). Hydrolysis of **9** (6.5×10^{-3} M) with 2 M HCl in refluxing ethanol gave a mixture of **10**, **12**, and **9** in a ratio of 17:73:10 (run 4). Hydrolysis of **9** under basic conditions using 0.05 M NH_3 proceeded at room temperature to provide a mixture of **10**, **12**, and **9** in a ratio of 5:71:24 (run 5). Hydrolysis of **13** (9.3×10^{-3} M) with 60% perchloric acid at 40°C in ethanol yielded a mixture of selenol **10** and triselenide **12** in a molar

TABLE 1 Hydrolysis of **9** and **13**

Run	*Substrate*	*Cat.-Solv./(v/v)*	*Conc. ($\times 10^{-3}$ M)*	*Temp., Time*	**10**:**12**:**9** *(or* ***13****)*[a]
1	**9**	60% $HClO_4$–EtOH–CH_2Cl_2 (2/5/0.7)	10	refl., 14 h	44:56:0
2	**9**	60% $HClO_4$–EtOH (2/5)	1.8	refl., 50 min	82:10:8
3	**9**	60% $HClO_4$–MeOH (2/5)	1.2	refl., 2 h	81:19:0
4	**9**	2 M HCl–EtOH (1/4)	6.5	refl., 5 h	17:73:10
5	**9**	0.05 M NH_3–EtOH (0.5/4)	4.2	r.t., 8 h	5:71:24
6	**13**	60% $HClO_4$–EtOH (1:2)	9.3	40°C, 3 h	54:46:0

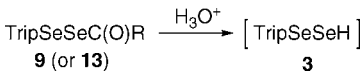
[a]Ratios of yields.

ratio of 54:46 (run 6).

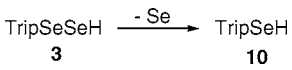


(4)

The effect of concentration on the hydrolysis of **9** is explained as follows: Selenenoselenoic acid **3** formed by hydrolysis (Eq. (5)) is unstable under the hydrolytic conditions and essentially loses the terminal selenium atom to give selenol **10** (Eq. (6)). However, when the hydrolysis is carried out under high concentration conditions, bimolecular reactions of **3** and between **3** and the starting **9** (or **13**) compete with the deselenation (Eq. (6)) to yield triselenide **12** (Eq. (7)). Under basic conditions, triselenide **12** was formed as the main product (run 5), indicating that the reaction of Eq. (7) is more favorable than that of Eq. (6) under the conditions. This result is in harmony with the fact that nucleophilicity of a selenol toward a selenium atom in a diselenide increases greatly in the selenolate ion form (RSe^-) compared with the selenol form (RSeH) [6,15,16]. An attempt to trap **3** with triphenyltin chloride under the basic conditions was unsuccessful.



(5)



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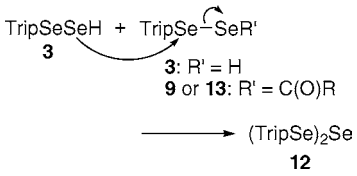

(7)

In summary, two diselenides **9** and **13** were synthesized by reaction of *Se*-9-triptycyl triptycene-9-selenoseleninate (**7**) with *p*-toluenecarboselenoic acid (**8**) and by reaction of triptycene-9-selenenoselenolate salt with *p*-toluoyl chloride or acetyl chloride, respectively. Hydrolysis of the two diselenides provided selenenoselenoic acid **3**, which was unstable under the conditions to decompose to triptycene-9-selenol (**10**) or to react with another molecule of **3** or the starting diselenide **9** or **13** yielding di-9-triptycyl triselenide (**12**).

EXPERIMENTAL

The melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were determined on Bruker AM400 or DRX400 (400 and 100.6 MHz, respectively) or AC300P (300 and 75.5 MHz, respectively) spectrometers using $CDCl_3$ as the solvent at 25°C. IR spectra were taken on a Hitachi 270-50 spectrometer. Mass spectra were determined on a JEOL JMS-DX303 or a JEOL JMS-700AM spectrometers operating at 70 eV in the EI mode. FAB MS was measured with *m*-nitrobenzyl alcohol as the matrix. Elemental analysis was performed by the Chemical Analysis Center of Saitama University. Column chromatography was performed with silica gel (70-230 mesh), and the eluent is shown in parentheses.

Synthesis of p-Toluoyl 9-Triptycyl Diselenide **9**

Sodium *p*-toluenecarboselenoate (43 mg, 0.194 mmol) was dissolved in acetone (18 mL) in a three-necked round-bottom flask equipped with a dropping funnel and a gas-inlet glass tube. HCl gas was introduced to the solution at 0°C until the color of the solution turned from yellow to pink. Selenoseleninate **7** (56 mg, 0.082 mmol) in dichloromethane (19 mL) was added through the dropping funnel, and the mixture was stirred for 1 h at 0°C. The mixture was warmed to room temperature and quenched with aqueous ammonium chloride. The mixture was extracted with dichloromethane, and the organic layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. The yellow residue was suspended in hexane, and compound **9** was collected by filtration. The filtrate was evaporated to dryness, and the residue was subjected to column chromatography (hexane/dichloromethane 3/1) to give another crop of **9**. The combined amount of **9** was 71.5 mg (83%). An analytical sample of **9** was obtained by recrystallization from a mixed solvent of hexane and dichloromethane.

9: Yellow crystals, mp 157–158°C decomp (hexane-CH_2Cl_2). ^{1}H NMR (300 MHz) δ 2.39 (s, 3H), 5.38 (s, 1H), 6.96–7.04 (m, 6H), 7.24 (d, J = 8.1 Hz, 2H), 7.34–7.40 (m, 3H), 7.60–7.66 (m, 3H), 7.85 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75.5 MHz) δ 21.8, 54.1, 63.6, 123.4, 124.2, 125.0, 125.7, 128.0, 129.7, 134.5, 144.7, 145.4, 145.5, 189.7; IR (KBr) ν 1694 cm^{-1} (C=O); MS (FAB) m/z 533 [$(C_{28}H_{20}O^{80}Se_2)^+ + 1$). Anal. Calcd for $C_{28}H_{20}OSe_2$: C, 63.41; H, 3.80. Found: C, 63.20; H, 3.66.

Synthesis of Acetyl 9-Triptycyl Diselenide **13**

t-BuLi (1.48 M in pentane, 0.10 mL, 0.148 mmol) was added to a solution of triptycene-9-selenol (**10**) (49.7 mg, 0.149 mmol) in THF (3 mL) under argon at 0°C, and the mixture was stirred for 10 min. The

solution of TripSeLi in THF was introduced through a Teflon tube to a suspension of elemental selenium (13.7 mg, 0.173 mmol) in THF (1 mL) under argon prepared in another flask. The mixture was stirred for 30 min at 0°C, and then acetyl chloride (0.02 mL, 0.28 mmol) was added. After stirring for 1 h, the mixture was quenched with water and extracted with dichloromethane. The extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness. A mixed solvent of hexane/dichloromethane (1/1) was added to the residue, and triselenide **12**, insoluble in the solvent, was removed by filtration (**12**: 35.7 mg, 64%). The filtrate was passed quickly through a column of silica gel (hexane/dichloromethane 1/1) to give **13**, which contained a small amount of triptycene. The crude **13** was washed with hexane to give the pure sample of **13** (9.3 mg, 25%).

In a similar manner, **9** was prepared from TripSeH (**10**) (49.1 mg, 0.147 mmol), *t*-BuLi (0.1 mL, 0.148 mmol), elemental selenium (12.8 mg, 0.162 mmol), and *p*-toluoyl chloride (0.02 mL, 0.15 mmol) in 24% yield (19.3 mg).

13: Yellow crystals, mp 197–200°C decomp (hexane-EtOH). ^{1}H NMR (300 MHz) δ 2.59 (s, 3H), 5.37 (s, 1H), 6.98–7.05 (m, 6H), 7.36–7.39 (m, 3H), 7.51–7.54 (m, 3H); ^{13}C NMR (100.6 MHz) δ 32.7, 54.1, 123.4, 124.0, 124.9, 125.8, 144.5, 145.4, 192.8; IR (KBr) ν 1739 cm^{-1} (C=O); MS *m/z* 456 [$(C_{22}H_{16}O^{80}Se_2)^+$]. HRMS: *m/z* 455.9531. Anal. Calcd for $C_{22}H_{16}O^{80}Se_2$: *M* 455.9536.

Hydrolysis of p-Toluoyl 9-Triptycyl Diselenide **9**

Diselenide **9** (41.1 mg, 0.0775 mmol) was dissolved in ethanol (5 mL) and dichloromethane (0.7 mL) under argon. To the solution was added 60% perchloric acid (2 mL) and the mixture was heated under reflux for 14 h. The mixture was cooled to room temperature and extracted with dichloromethane. The extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness. The ^{1}H NMR of the residue showed the formation of selenol **10** and triselenide **12** in a molar ratio of 61:39 based on the integral ratio, indicating that the ratio of yields (**10**:**12**) was 44:56.

Hydrolysis of Acetyl 9-Triptycyl Diselenide **13**

Ethanol (2 mL) and 60% perchloric acid (1 mL) was added to diselenide **13** (12.8 mg, 0.028 mmol) under argon, and the mixture was stirred at 40°C for 3 h. The mixture was extracted with dichloromethane, and the extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness. The ^{1}H NMR of the residue showed the formation of selenol **10** and triselenide **12** in a molar ratio of 70:30 based on the integral ratio, indicating that the ratio of yields (**10**:**12**) was 54:46.

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