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## SYNTHESES WITH DIKETO SELENIDES

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Abstract We report a) a modified synthesis of diketo selenides, b) preparation of 2,5-diacylselenophenes by condensation of diketo selenides with glyoxal, c) preparation of poly-substituted selenophenes by intramolecular reductive coupling reaction of diketo selenides with low-valent titanium reagent under controlled conditions (0°C) followed by dehydration of the resulting 3,4-dihydroxyselenolanes, and d) formation of 2,5-dihydroselenophenes and 1,3-dienes by treatment of diketo selenides with the low-valent titanium reagent in refluxing tetrahydrofuran.

We have been investigating syntheses with diketo sulfides.<sup>1</sup> In this connection we now turned to syntheses with diketo selenides. Herein we report a modified synthesis of diketo selenides and some results of the synthesis with diketo selenides.

### 1) PREPARATION OF DIKETO SELENIDES

Diketo selenide dichlorides (1) were prepared by reaction of selenium oxychloride with 2 equiv. of ketones in anhydrous ether.<sup>2</sup> The reaction is complete on standing overnight at room temperature and 1 precipitates in excellent yields as practically pure near-white crystals which are scarcely soluble in ordinary organic solvents. Only two diketo selenides were previously prepared by dechlorination of 1.<sup>3</sup> The reported method, however, requires prolonged refluxing (3 days) of 1 with zinc powder in a large amount of hazardous carbon disulfide. We now found that portion-

wise addition of 1 to a stirred two-phase mixture of an aqueous solution of sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) and benzene affords diketo selenides 2 in good yields. Results are summarized in Table 1.

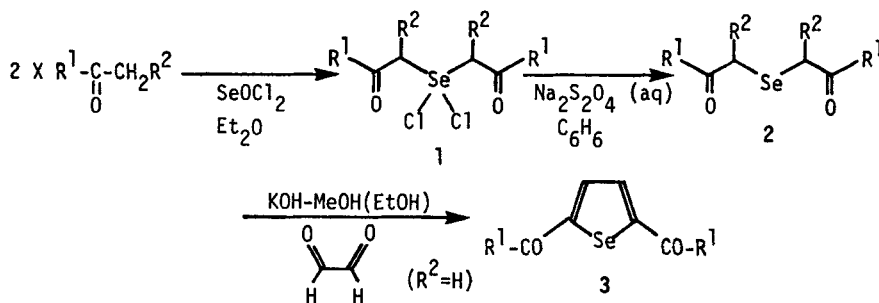


Table 1. Preparation of Diketo Selenide Dichlorides (1), Diketo Selenides (2), and 2,5-Diacylselenophenes (3)

$\text{R}^1$	$\text{R}^2$	Yield of <u>1</u> (%)	Yield of <u>2</u> <sup>a</sup> (%)	Yield of <u>3</u> <sup>b,c</sup> (%)
$\text{C}_6\text{H}_5$	H	99	89	73
4-Cl $\text{C}_6\text{H}_4$	H	71	77	70 <sup>d</sup>
4-Me $\text{C}_6\text{H}_4$	H	97	93	69
4-MeOC $\text{C}_6\text{H}_4$	H	94	97	45
1-naphthyl	H	83	99	65 <sup>d</sup>
2-thienyl	H	88	89	58
$\text{CH}_3$	H	83	56	13 <sup>e</sup>
$(\text{CH}_3)_3\text{C}$	H	77	95	13
$\text{C}_6\text{H}_5$	$\text{CH}_3$	65	99 <sup>f</sup>	

a) Yields based on crude products containing a small amount of the original ketones as impurity. b) 2.5 Equiv. of glyoxal monomer was used unless otherwise stated. c) Methanol was used as solvent for condensation. d) Ethanol was used as solvent. e) 5 Equiv. of glyoxal monomer was used. f) A mixture of meso- and d,l-isomers.

## 2) PREPARATION OF 2,5-DIACYLSELENOPHENES

The following is a typical procedure for the preparation of 2,5-diacylselenophenes (3). Glyoxal trimeric dihydrate (0.67 g, 9.6 mmol) was heated in boiling methanol (30 ml) for 1 h to obtain a homogeneous solution of glyoxal monomer. To this hot solution was added 1.27 g (4 mmol) of diphenacyl selenide. The mixture was refluxed and to this was added a solution of potassium hydroxide (244 mg, 4.3 mmol) in methanol (10 ml) during 10 min. The resulting mixture was refluxed for 0.5 h and cooled. The crystalline precipitate was collected and washed with methanol until the washings became colorless. 2,5-Dibenzoylselenophene thus obtained contains selenium powder as impurity, which was removed by washing with methylene chloride. Selenium is practically insoluble in methylene chloride, while the selenophene is soluble, and thus evaporation of the solvent from the washing leaves the selenophene (0.87 g, 64%) in a pure form. If necessary, a further amount of the selenophene (9%) is obtained by purifying the original filtrate and washings in an appropriate way. Results obtained with a variety of diketo selenides are summarized in Table 1.

## 3) PREPARATION OF POLYSUBSTITUTED SELENOPHENES

We have shown that the intramolecular reductive coupling reaction of diketo sulfides by a low-valent titanium reagent under controlled conditions (0 °C) gives good yields of 3,4-dihydroxythiolanes, which are converted to the corresponding thiophenes nearly quantitatively by acid-catalyzed dehydration.<sup>1b</sup> We now report that application of the same procedure to diketo selenides provides a convenient method for the preparation of selenophenes.

To a stirred mixture of a low-valent titanium reagent, prepared from titanium(IV) chloride (15 mmol) and zinc powder (30 mg-atoms) in THF (40 ml),<sup>4</sup> was added a solution of diphenacyl selenide (5 mmol) in THF (20 ml) at ca. -15 °C. After the completion of the addition, the mixture was stirred at ca. 0 °C for 3 h.

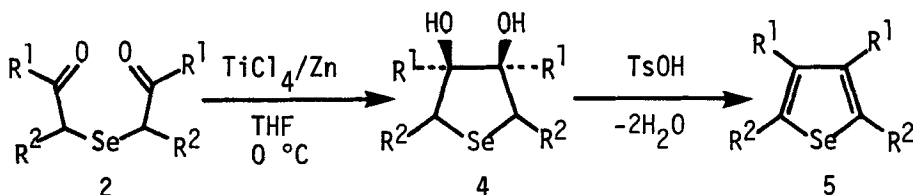


Table 2. Preparation of Selenophenes (5) from Diketo Selenides (2)

R <sup>1</sup>	R <sup>2</sup>	Yield (%)	
		2 $\longrightarrow$ 4	4 $\longrightarrow$ 5
C <sub>6</sub> H <sub>5</sub>	H	60	97
4-MeC <sub>6</sub> H <sub>4</sub>	H	48	97
4-ClC <sub>6</sub> H <sub>4</sub>	H	70	97
2-thienyl	H	56	98
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	55	94

Alkaline workup of the mixture followed by chromatographic purification afforded *cis*-3,4-dihydroxy-3,4-diphenylselenolane in 60% yield. *cis*-Configuration of the selenolane was established by deselenation with Raney nickel in boiling ethanol, which afforded *meso*-2,3-dihydroxy-2,3-diphenylbutane (44%) and *meso*-2,3-diphenylbutane (28%). Heating the selenolane with a catalytic amount of *p*-toluenesulfonic acid in refluxing toluene for 1 h produced 3,4-diphenylselenophene in 97% yield. In a similar way several selenophenes were synthesized as shown in Table 2.

#### 4) FORMATION OF 2,5-DIHYDROSELENOPHENES AND 1,3-DIENES FROM DIKETO SELENIDES BY REDUCTION WITH LOW-VALENT TITANIUM REAGENT

We have recently reported that the intramolecular reductive coupling reaction of diketo sulfides by the low-valent titanium reagent in refluxing THF or dioxane gives 2,5-dihydrothiophenes in good yields.<sup>1a</sup> We now report that treatment of diketo selenides by the same reagent under similar conditions leads to 2,5-dihydro-

selenophenes (6) and 1,3-dienes (7) in comparable yields.

To a refluxing mixture of the foregoing titanium reagent, prepared from titanium(IV) chloride (15 mmol) and zinc powder (30 mg-atoms) in THF (40 ml), was added dropwise a solution of diphenacyl selenide (5 mmol) in THF (20 ml). After the completion of the addition, the mixture was refluxed for 2 h. Chromatographic workup of the mixture afforded 2,5-dihydro-3,4-diphenylselenophene (6a, 16%), 2,3-diphenyl-1,3-butadiene (7a, 31%), and 3,4-diphenylselenophene (1.5%). Dihydroselenophene 6a is relatively thermally stable and does not extrude selenium to give the diene either under the reaction conditions or in refluxing toluene. Treatment of 6a with  $\text{SO}_2\text{Cl}_2$  affords the dichloride 8, which eliminates hydrogen chloride, when heated at 150°C, to produce 3,4-diphenylselenophene in good overall yield.

In a similar way several diketo selenides were subjected to reduction. Results are summarized in Table 3. In every case 6 and 7 were produced in comparable yields. In entry 2, when the meso isomer was subjected to the reduction, cis-2,5-dihydro-2,5-dimethyl-3,4-diphenylselenophene was exclusively formed, while the ratio of E,E- and E,Z-isomers of 3,4-diphenyl-2,4-hexadiene was 97:3.

The proposed intermediate for the olefin-forming reaction from carbonyl compounds by reduction with low-valent titanium reagents involves a cyclic titanium(II) compound.<sup>5</sup> The corresponding intermediate is 9 in the present case. Formation of this type of cyclic intermediate explains the exclusive formation of cis-3,4-dihydroxyselenolanes under the controlled conditions. Elimination of titanium dioxide from 9 affords 2,5-dihydroselenophenes 6, while simultaneous extrusion of titanium dioxide and selenium from 9 produces 1,3-dienes 7. Both processes presumably occur competitively. The latter process, which was rarely observed with diketo sulfides, stems from weaker bond strength of the C-Se bond compared with the C-S bond and predominantly occurs in a dis-

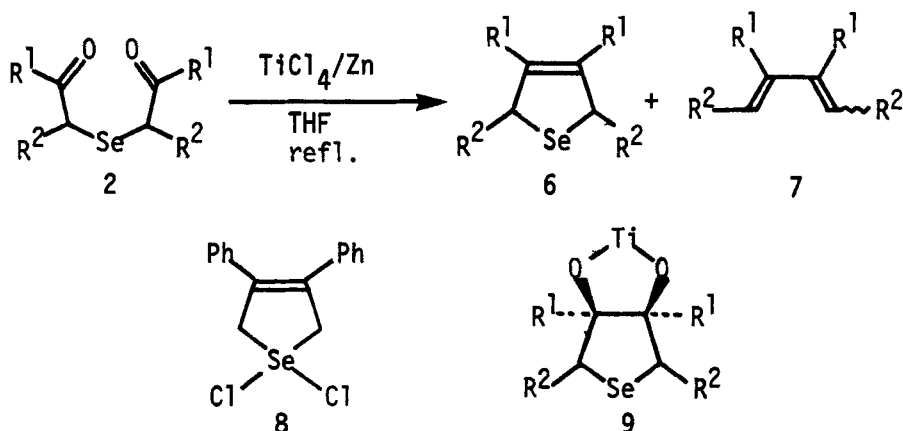


Table 3. Formation of 2,5-Dihydroselenophenes (**6**) and 1,3-Dienes (**7**) by Reductive Coupling Reaction of Diketo Selenides (**2**)

Entry	R <sup>1</sup>	R <sup>2</sup>	Yield of <b>6</b> (%)	Yield of <b>7</b> (%)
1	C <sub>6</sub> H <sub>5</sub>	H	16	31
2	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	20	35
3	4-MeC <sub>6</sub> H <sub>4</sub>	H	13	26
4	4-ClC <sub>6</sub> H <sub>4</sub>	H	30	36
5	2-thienyl	H	24	28

rotatory manner on the basis of the observed stereochemistry with the meso isomer in entry 2.

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