Formation of 2,5-Dihydroselenophenes and 1,3-Dienes from Diketo Selenides by Reduction with Low-valent Titanium Reagents

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Reduction of a series of diketo selenides with a low-valent titanium reagent affords 2,5-dihydroselenophenes and 1,3-dienes in comparable yields.

We recently reported that the intramolecular reductive coupling of diketo sulphides by a low-valent titanium reagent gives 2,5-dihydrothiophenes in good yields.[1] We now report that treatment of diketo selenides (**1**) with the same reagent leads to 2,5-dihydroselenophenes (**2**) and 1,3-dienes (**3**) in comparable yields.

To a refluxing mixture of a low-valent titanium reagent, prepared from titanium(IV) chloride (15 mmol) and zinc powder (30 mmol),[2] in tetrahydrofuran (40 ml) a solution of diphenacyl selenide (**1a**) (5 mmol) in tetrahydrofuran (20 ml) was added dropwise. The mixture was then refluxed for 2 h. Chromatographic workup of the mixture afforded 2,5-dihydro-3,4-diphenylselenophene (**2a**) (16%), 2,3-diphenylbuta-1,3-diene (**3a**) (31%), and 3,4-diphenylselenophene (1.5%). When the reaction was carried out at 0 °C, *cis*-3,4-dihydroxy-3,4-diphenylselenolane (**4**) was obtained in 60% yield.† Treatment of (**4**) by the low-valent titanium reagent in refluxing tetrahydrofuran (THF) for 2 h afforded (**2a**) (20%) and (**3a**) (33%) with 35% recovery of (**4**). Compound (**2a**) is a thermally stable crystalline compound and does not extrude selenium to yield the diene (**3a**) either under the reaction conditions or in refluxing toluene. Treatment of (**2a**) with sulphuryl chloride affords the dichloride (**5**), which, when heated at 150 °C, eliminates hydrogen chloride to give 3,4-diphenylselenophene in good overall yield.

In a similar way, several diketo selenides (**1**) were subjected to the reduction with similar results which are summarized in

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† *cis*-Configuration of (**4**) was established by deselenation with Raney nickel, which afforded *meso*-2,3-dihydroxy-2,3-diphenylbutane (44%) and *meso*-2,3-diphenylbutane (28%).

Table 1. Formation of 2,5-dihydroselenophenes (**2**) and 1,3-dienes (**3**) by reduction of diketo selenides (**1**) with a low-valent titanium reagent.

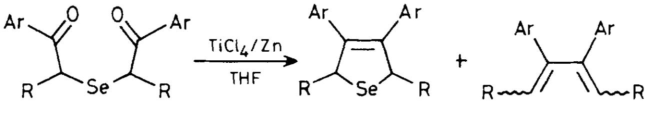
Entry[a]	Ar	R	Yield of (**2**)/ %	Yield of (**3**)/ %
1[b]	Ph	H	16	31
2[c,d]	Ph	Me	20	35
3[b]	4-MeC$_6$H$_4$	H	13	26
4[b]	4-ClC$_6$H$_4$	H	30	36
5[b]	thien-2-yl	H	24	28

[a] The mixture was refluxed for 2 h after addition of a solution of (**1**), unless otherwise stated. [b] A small amount of corresponding 3,4-diarylselenophenes was obtained (1—2%). [c] Refluxed for 4 h. [d] 3,4-Dihydroxy-2,5-dimethyl-3,4-diphenyl-selenolane (9%) was also obtained.

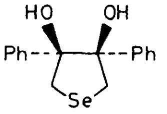
Table 1. In entry 2, when the *meso*-isomer (m.p. 92 °C) was subjected to the reduction, *cis*-2,5-dihydro-2,5-dimethyl-3,4-diphenylselenophene (**2b**) was exclusively formed, whilst the ratio of (*E*,*E*)- to (*E*,*Z*)-isomers of 3,4-diphenylhexa-2,4-diene (**3b**) was 97 : 3.

The proposed intermediate for the alkene-forming reaction from carbonyl compounds by reduction with low-valent titanium reagents involves a cyclic titanium(II) compound.[3] The corresponding intermediate is (**6**) in the present case. Elimination of titanium dioxide and simultaneous extrusion of titanium dioxide and selenium from (**6**) presumably occur competitively to give (**2**) and (**3**), respectively. The latter process, which was rarely observed with diketo sulphides,[1] probably stems from the weaker bond strength of the C–Se bond compared with the C–S bond and predominantly occurs in a disrotatory manner on the basis of the observed stereochemistry with the *meso*-isomer in entry 2.

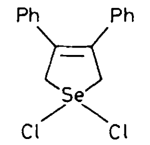
Although the synthesis and synthetic utility of 2,5-dihydrothiophenes and their 1,1-dioxides have been relatively well documented, no practical method for the synthesis of 2,5-dihydroselenophenes is available.[4,5] Although yields are low, this preparative method provides the only promising route to this heterocyclic ring.



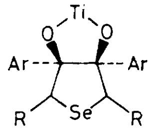
(**1**) (**2**) (**3**)



(**4**)



(**5**)



(**6**)

a; Ar = Ph, R = H
b; Ar = Ph, R = Me
c; Ar = 4-MeC$_6$H$_4$, R = H
d; Ar = 4-ClC$_6$H$_4$, R = H
e; Ar = thien-2-yl, R = H

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References

1 J. Nakayama, H. Machida, and M. Hoshino, *Tetrahedron Lett.*, 1985, **26**, 1981.
2 T. Mukaiyama, T. Sato, and J. Hanna, *Chem. Lett.*, 1973, 1041.
3 E. J. Corey, R. L. Danheiser, and S. Chandrasekaran, *J. Org. Chem.*, 1976, **41**, 260.
4 To our knowledge, 2,2′-bis(2,5-dihydro-2-carboxyselenophene), which was formed along with other products by electrochemical reduction of 2-carboxyselenophene, is the only reported example of this ring system; V. P. Gultyai, T. G. Konstantinova, A. M. Moiseenlov, V. P. Litvinov, and A. Konar, *Chem. Scr.*, 1982, **19**, 95.
5 J. Nakayama, M. Shibuya, and M. Hoshino, *Heterocycles*, 1987, **26**, 909.