

Reaction of Arylselenium Titanocene Complexes with Diaryl Iodonium Salts----a Convenient Synthesis of Unsymmetrical Diarylselenides

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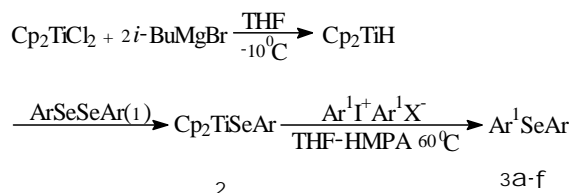
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Abstract: The diaryldiselenides reacted with titanocene hydride (Cp_2TiH) generated from $\text{Cp}_2\text{TiCl}_2/i\text{-BuMgBr}$ to give arylselenium complexes of titanocene. They reacted readily with diaryliodonium salt to give unsymmetrical diarylselenides.

Keywords: Diarylselenide, diaryl iodonium salt, arylselenium titanocene complexes, synthesis.

Unsymmetrical diaryl selenides are important intermediates in the synthesis of a wide variety of organic compounds. A number of methods of synthetic routes to unsymmetrical diaryl selenides are available. They include the reactions of diazonium salts with alkali arylselenoates¹, diaryl diselenides with Grignard reagents², arylselenium bromide with diaryl mercuric, copper (I)³ or nickel (II)⁴ catalyzed arylation of areneselenoates by aryl halides, aryl arylsulfones with alkaline areneselenoates⁵ and arylselenation of electron-rich aromatic compounds with (phenylseleno) dimethylsulfonium tetrafluoro-borate⁶. However, some of these methods suffer from disadvantages such as harsh reaction conditions or lower yields. We now report a new method for the synthesis of unsymmetrical diarylselenides.

We recently found that titanocene hydride (Cp_2TiH)⁷ generated from the reaction of Cp_2TiCl_2 with *i*-BuMgBr, readily reduced diaryldiselenides to yield arylselenium complexes of titanocene (Cp_2TiSeAr). Cp_2TiSeAr has good nucleophilicity and can be thought as an equivalent of arylselenenyl anion. Cp_2TiSeAr reacted with acyl halides or anhydrides to afford selenoesters⁸. In this paper we tried to study its reactivity with haloarenes. However, the experiment showed that they cannot react with haloarenes smoothly. Considering that diaryl iodonium salt is a highly reactive arylating reagent, which can be regarded as an equivalent of aryl cation, we study the reaction of Cp_2TiSeAr with diaryl iodonium salts. The experiment showed that Cp_2TiSeAr (1.0 mmol) reacted with diaryl selenides in high yields. The results are summarized in **Table 1**.

**Table 1** Unsymmetrical Diaryl Selenides (**3a-f**)

Product	Ar	Ar ¹	mp. °C (lit)	Yield (%)
3a	<i>p</i> -CH ₃ C ₆ H ₄	Ph	Oil	78
3b	<i>m</i> -CH ₃ C ₆ H ₄	Ph	Oil	70
3c	<i>p</i> -CH ₃ OC ₆ H ₄	Ph	Oil	73
3d	<i>p</i> -ClC ₆ H ₄	Ph	Oil	69
3e	<i>p</i> -ClC ₆ H ₄	<i>p</i> -CH ₃ C ₆ H ₄	71-72(72-73) ⁹	75
3f	<i>p</i> -BrC ₆ H ₄	<i>p</i> -CH ₃ C ₆ H ₄	77-79(80-81) ⁹	75

* The **3a-3f** were identified by IR, ¹H NMR and elemental analyses.

The above method provides a new path for the synthesis of unsymmetrical diarylselenides. Moreover, it has the advantages of simple procedure, mild reaction conditions and good yields.

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