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A NEW METHOD FOR THE REDUCTIVE CLEAVAGE OF Se-Se BOND BY TITANOCENE DICHLORIDE ISOBUTYL-MAGNESIUM BROMIDE SYSTEM AND ITS APPLICATION IN SYNTHESIS OF SELENOESTER

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Abstract: The reduction of diaryldiselenides by $Cp_2TiCl_2/2i$ -BuMgBr/THF led to arylselenium complex of titanocene ($Cp_2TiSeAr$). This species reacts smoothly with acidic anhydrides to give selencesters.

Organoselenium compounds have attracted considerable interest as reagents and intermediates in organic synthesis¹. A convenient and general method to introduce a selenium group into organic molecules is the reaction of a metal selenoate with approriate electrophiles. Diaryl diselenides are important intermediates due to their stability aganist air and water. When they are reducted, the nucleophilic selenoates are obtained. Reduction of diselenides usually uses NaBH₄ as reductant². Recently reductive cleavage of Se-Se bond by SmI₂ has been wildly investigated and there have been many reports in the respects of its applies in synthesis. Now we wish to describe a new method for reducing diaryldiselenides by $Cp_2TiCl_2/2i$ -BuMgBr/THF system and use of it for the conversion of acidic anhydrides to their corresponding arylselenoesters.

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Titanocene hydride (Cp₂TiH) derived from the reaction of Cp₂TiCl₂ with i-BuMgBr is a very strong reductant⁴. We found that under mild condition Cp₂TiH readily reducted cleavage of diaryldiselenides to give corresponding arylselenium complex of titanocene (Cp₂TiSeAr). Cp₂TiSeAr in THF has good stability. it can be stored for a month under nitrogen at room temperature. It is an efficient nucleophile and it reacts with acidic anhydrides in THF-HMPA to afford selenoesters in good yields. The results were summarized in Table 1.

Cp₂TiCl₂/2*i*-BuMgBr/THF

 $\begin{array}{c} & & \downarrow -10-0^{\circ}C \\ \text{ArSeSeAr} \xrightarrow{\text{Cp}_{2}\text{TiH}} \text{Cp}_{2}\text{TiSeAr} \xrightarrow{\text{(RCO)}_{2}O} \text{RCoSeAr} \\ \text{1a-c} & \text{2a-c} & \text{3a-f} \end{array}$

R m. P°C or b. p°C/mmHg (lit °C) product Ar Yield* 3a Ph CH₃ oil 112 - 114/2067 3b Ph CH₂CH₃ oil 122 - 126/1860 39-40[40]6 Ph Ph 58 3c 71-72[70-71] 3d p-CH₃C₆H₄ Ph 62 98-100[97-97]⁷ p-CH₃OC₆H₄ Ph 3e 55 3f p-CH₃OC₆H₄ CH₃ oil 96 - 100/2065

Table 1 Synthesis of selencesters 3a-f

' yield of isolated pure product based on 1a-c

2e,2f recrystallized from hexane, 2f recrystallized from hexane/ethanol (1:1)

There have been many methods of synthesizing selencesters⁵. However, most of these methods have certain disadvantages such as harsh reaction conditions, laborious manipulation or obtaining lower yield. The present method has the advantages of easy availability of starting materials, mild reaction conditions, convenient manipulation and moderate yields.

Experiments and materials

¹H NMR spectra were recorded on PMX-60 spectrometer, using CDCl₃ as the solvent with TMS as an internal standard. IR spectra were determined on PE-683 spectrophotometer. Melting point were uncorrected. Tetrahydro furan was distilled from sodium benzophenone. Commercial HMPA was dried over 4A molecular sieves. All reactions were carried out under pure nitrogen.

A representative procedure for the synthesis of arylselenium complexs of titanocene 2a-c

To the suspension of 2. 5g(10 mmol) finelly ground titanocene dichloride in 50 ml THF was added a THF solution of i-BuMgBr (1. 0m, 20 ml) for 30 minutes at -10° C. The reaction mixture turned out to be brown-blackish with a complete dissolution and further was stirred 20 minutes at 0°C. The diselenide (5. 0 mmol) was added to the reaction mixture. The solution became immediately deep blue. The mixture was stirred for 1h at room temperature. This solution could be stored at room temperature under a positive pressure of pure nitrogen for periods of up to on month. If the solution was stored in the refrigerator with an accompanying loss in reagent efficacy. Aliquots were withdrawn as need with dry pure nitrogenpurged syrings. The concentration of the reagent was assumed to be approximately the same as the inifial solution.

A representative procedure for the synthesis of selenoesters:

To a solution of acidic anhydride (2.0 mmol) in 2 ml HMPA was added 10 ml (2.0 mmol) of $Cp_2TiSeAr$ salution in THF by syringe, the mixture was

stirred at room temperature for 30 minutes. then further stirred at 40°C for 2 h. Finally the deep blue disappeared thoughfully and the mixture turned out to be red-brown. The mixture was diluted with ether (40 ml). Then washed three times with brine (60 ml \times 3). The organic layer was dried over MgSO₄ and evaporated to give the crude products. The crude products were purified by crystal-lization or by distillation.

Compord 3a $\nu_{max}(film)/cm^{-1}$ 3050,1740,1600,1105. σ_{H} 7.40(m,5 H),2.37 (s,3 H).

Compord **3b** ν_{max} (film)/cm⁻¹ 3045,2998,1735,1595,900. σ_{H} 7. 33(m,5 H), 2. 39(q,2 H),1.07(t,3 H).

Compond **3c** ν_{max} (KBr)/cm⁻¹ 3050,1690,1610,1100, σ_{H} 7.82(m,2 H),7.40 (m,8 H).

Compord 3d ν_{max} (KBr)/cm⁻¹ 3004,1695,1590,1495. σ_{H} 7.20–7.75(m,9 H), 2.33(s,3 H).

Compond **3e** ν_{max} (KBr)/cm⁻¹ 3045,2990,1685,1595,1495,1020. $\sigma_{\rm H}$ 6.7–7.5 (m,9 H),3.68(s,3 H).

Compord **3f** ν_{max} (film)/cm⁻¹ 2995,1735,1600,1495,1250. σ_{H} 7. 23(d,2 H), 6. 27(d,2 H), 3. 70(s,3 H), 2. 38(s,3 H).

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