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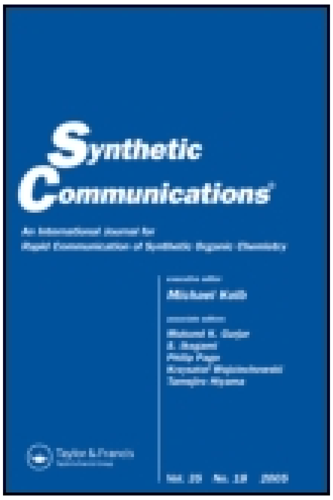

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

SYNTHESIS OF UNSYMMETRICAL DIARYLSELENIDES FROM ARYLSELENIUM COMPLEXES OF TITANOCENE AND DIARYL IODONIUM SALTS

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Published online: 16 Aug 2006.

To cite this article: Xiang Huang , Lu-Ling Wu & Xin-Hua Xu (2001) SYNTHESIS OF UNSYMMETRICAL DIARYLSELENIDES FROM ARYLSELENIUM COMPLEXES OF TITANOCENE AND DIARYL IODONIUM SALTS, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:12, 1871-1874, DOI: 10.1081/SCC-100104337

To link to this article: http://dx.doi.org/10.1081/SCC-100104337

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SYNTHETIC COMMUNICATIONS, 31(12), 1871–1874 (2001)

SYNTHESIS OF UNSYMMETRICAL DIARYLSELENIDES FROM ARYLSELENIUM COMPLEXES OF TITANOCENE AND DIARYL IODONIUM SALTS

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Diary selenides are important intermediates and a variety of synthetic routes to unsymmetrical diaryl selenides are available. They include the reactions of diazonium salts with alkali aryselenoates,[1] diaryl deselenides with Grignard reagents,[2] arylselenium bromide with diaryl mercurical, copper(I)[3] or nickel(II)[4] catalyzed arylation of areneseslenoates by aryl iodides or bromides, aryl arylzo sulfones with alkaline areneselenoates,[5] arylselenation of electron-rich aromatic compounds with (phenylseleno)-dimethylsulfonium tetrafluoroborate[6] and photo-stimulated S_{RN}**1** reaction of phenyl selenides with haloarenes.[7] However, some of these methods suffer from disadvantages such as the use of expensive or less easily available reagents, 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)[8] generated from the reaction of Cp_2TiCl_2 with *i*-BuMgBr under mild conditions, readily reduced diaryldiselenides to yield the corresponding arylselenium complexes of titanocene ($Cp_2TiSeAr$). They can be isolated and stored in THF for a month under

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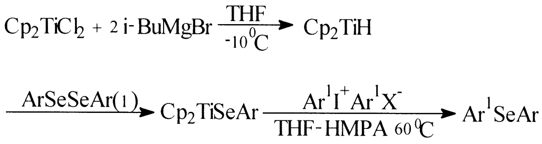
* Corresponding author.

nitrogen at room temperature. $Cp_2TiSeAr$ has good nucleophilicity and can be thought as an equivalent of arylselenenyl anion. We have reported that they reacted with acyl halides or anhydrides to afford a convenient method for the synthesis of selenoesters.[9] 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 high 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 $Cp_2TiSeAr$ reacted readily with diaryliodonium salts in THF/HMPA at 60°C to give the unsymmetrical diaryl selenides in high yields. The results are summarized in Table I.

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.



2

3a-f

Table I. Unsymmetrical Diaryl Selenides (**3a-f**)

Product	Ar	Ar^1	M.p.°C(lit.)	Yield (%)
3a	p-$CH_3C_6H_4$	Ph	oil	78
3b	m-$CH_3C_6H_4$	Ph	oil	70
3c	p-$CH_3OC_6H_4$	Ph	oil	73
3d	p-ClC_6H_4	Ph	oil	69
3e	p-ClC_6H_4	p-$CH_3C_6H_4$	71–72(72–73)[10]	75
3f	p-BrC_6H_4	p-$CH_3C_6H_4$	77–79(80–81)[10]	75

* Yields based on **1**.

EXPERIMENTAL

^1H NMR spectra were recorded on AZ-300 spectrometer, using $CDCl_3$ as the solvent with TMS as internal standard. IR spectra were determined on PE-683 spectrophotometer. Melting point are uncorrected. Tetrahydrofuran was distilled from sodium benzophenone. Commercial HMPA was dried over calcium hydride, distilled *in vacuo* and stored over 4A molecular sieves. All reactions were carried out under nitrogen.

Typical Procedure for the Synthesis of Arylselenium Complexes of Titanocene (2): To the suspension of 2.5 g (10 mmol) of finely ground titanocene dichloride in 50 ml THF was added a THF solution of *i*-BuMgBr (1.0 M, 20 ml) for 30 minutes under stirring at −10°C. The reaction mixture turned blackish-brown with a complete dissolution of titanocene and was further stirred 20 minutes at 0°C. The diaryldiselenide (5.0 mmol) was added to the reaction mixture. The solution immediately became deep blue. The mixture was stirred for 1 hour at room temperature. This solution was stored at room temperature under a positive pressure of pure nitrogen and used in the preparation of unsymmetrical diarylselenides.

A Representative Procedure for the Synthesis of Unsymmetrical Diarylselenides (3a–f): To a solution of the diaryliodonium salt (1.0 mmol) in 2.0 ml HMPA was added 5.0 ml (1.0 mmol) of $Cp_2TiSeAr$ solution in THF by syringe. The mixture was stirred at room temperature for 30 minutes, then stirred further for 2 h at 60°C, finally the deep blue disappeared completely and the mixture turned red-brown. The reaction mixture was diluted with dilute aqueous HCl (20 ml), and the aqueous layer was extracted with ether (3 × 20 ml). The combined organic phase was washed with a saturated aqueous Na_2CO_3 solution and brine and dried ($MgSO_4$) and the solvent was evaporated. The residue was subjected to preparative TLC on silica gel using light petroleum-ether as eluent (30:1).

4-Methylphenyl phenyl selenide **3a**: IR(film): 3080, 2930, 1580, 1480, 1440, 1060, 1020, 800, 730, 685, 660 cm^{-1}; ^1H NMR: δ 2.28 (s, 3H), 7.10–7.51 (m, 9H); Calcd. for $C_{13}H_{12}Se$: C, 63.16, H, 4.89. Found: C, 63.20, H, 4.87.

3-Methylphenyl phenyl selenide **3b**: IR(film): 3075, 2930, 1580, 1480, 1445, 1060, 1020, 1090, 830, 770, 730, 680 cm^{-1}; ^1H NMR: δ 2.30 (s, 3H), 7.07–7.60 (m, 9H); Calcd. for $C_{13}H_{12}Se$: C, 63.16, H, 4.89. Found: C, 63.14, H, 4.85.

4-Methoxyphenyl phenyl selenide **3c**: IR(film): 3085, 2885, 1605, 1495, 1480, 1250 cm^{-1}; ^1H NMR: δ 3.73 (s, 3H), 7.13–7.42 (m, 5H); Calcd. for $C_{13}H_{12}OSe$: C, 59.32, H, 4.60. Found: C, 59.50, H, 4.56.

4-Chlorophenyl phenyl selenide **3d**: IR(film): 3080, 2930, 1680, 1480, 1440, 1390, 1090, 1010, 810, 730, 685 cm^{-1}; ^1H NMR: δ 7.12–7.61 (m); Calcd. for $C_{12}H_9ClSe$: C, 53.86, H, 3.39. Found: C, 53.75, H, 3.32.

4-Chlorophenyl 4-methylphenyl selenide **3e**: IR(film): 3080, 2930, 1495, 1475, 1390, 1250, 1090, 1010, 810 cm^{-1}; ^1H NMR: δ 2.29 (s, 3H), 7.05–7.45 (m, 8H).

4-Bromophenyl 4-methylphenyl selenide **3f**: IR(film): 3080, 2930, 2860, 1495, 1475, 1390, 1070, 1010, 810 cm^{-1}; ^{1}H NMR: δ 2.28 (s, 3H), 6.91–7.30 (m, 8H).

ACKNOWLEDGMENT

Project 29672008 was supported by National Nature Science Foundation of China.

REFERENCES

1. Keimatsu, L.S. and Yokota, K. J. Pharma. Soc. Japan **1930**, *50*, 531.
2. Campbell, T.W. and McCullough, J.D. J. Am. Chem. Soc. **1945**, *67*, 1965.
3. Osuka, A.; Ohmasa, N. and Suzuki, H. Synthesis **1982**, 857.
4. Cristau, H.J.; Chabaud, B.; Labaudiniere, R. and Christol, E. Organometallics **1985**, *4*, 657.
5. Evera, M.J.; Christiaens, L.E. and Renson, M.J. J. Org. Chem. **1986**, *51*, 5196.
6. Gassman, P.G.; Miura, A. and Miura, T. ibid. **1982**, *47*, 951.
7. Pierini, A.B. and Rossi, R.A. ibid. **1979**, *44*, 4667.
8. Gao, Y. and Sato, F. Chem. Commun. **1995**, 659.
9. XU, X.-H. and Huang, X. Synth. Commun. **1997**, *27*, 3797.
10. Greenberg, B.; Gould, E.S. and Burlant, W. J. Am. Chem. Soc. **1956**, *78*, 4028.

Received in the USA August 30, 2000

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