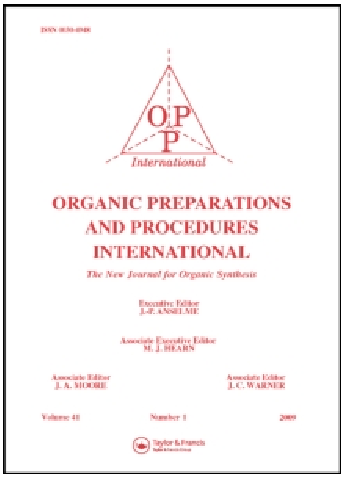


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

AN EFFICIENT, ONE-POT SYNTHESIS OF ALKYL ARYLSELENOFORMATES USING THE ZINC-RUTHENIUM CHLORIDE SYSTEM IN AQUEOUS MEDIA

Barahman Movassagh[a]; Ameneh Tatar[a]
[a] Department of Chemistry, K. N. Toosi University of Technology, Tehran, IRAN

To cite this Article Movassagh, Barahman and Tatar, Ameneh(2008) 'AN EFFICIENT, ONE-POT SYNTHESIS OF ALKYL ARYLSELENOFORMATES USING THE ZINC-RUTHENIUM CHLORIDE SYSTEM IN AQUEOUS MEDIA', Organic Preparations and Procedures International, 40: 5, 477 — 481

To link to this Article: DOI: 10.1080/00304940809458110
URL: http://dx.doi.org/10.1080/00304940809458110

(**1991**); (c) *Heterocyclic Chemistry,* T. L. Gilchrist, 2nd Ed. John Wiley & Sons Inc., 181 (1992).

20. R. G. Pearson, H. Sobel and J. Songstad, *J. Am. Chem. Soc.*, **90**, 319 (1968).

21. I. Yavari, A. Zonouzi and R. Hekmat- Shoar, *Tetrahedron Lett.*, **39**, 3841 (1998).

****

AN EFFICIENT, ONE-POT SYNTHESIS OF ALKYL ARYLSELENOFORMATES USING THE ZINC-RUTHENIUM CHLORIDE SYSTEM IN AQUEOUS MEDIA

Submitted by (09/02/07)

Barahman Movassagh* and Ameneh Tatar

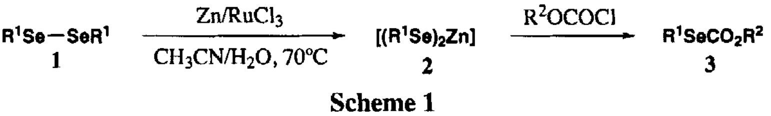
Department of Chemistry, K. N. Toosi University of Technology,
P. O. Box 16315-1618, Tehran, IRAN
E-mail: bmovass1178@yahoo.com

The chemistry of organoselenium compounds has been of growing interest because of the many synthetic applications of these compounds.[1] For example, selenoformates are used for the synthesis of γ- and δ-lactones through the intramolecular addition of alkoxycarbonyl radicals onto carbon-carbon multiple bonds.[2] Over the last three decades, many investigators have described important chemical transformations that were efficiently achieved using organoselenium reagents. Although numerous reports on the synthesis of organoselenium compounds have already been published,[3,4] most of them with the exception of three recent reports,[5] usually require the handling of unstable reagents, strongly acidic or basic reaction conditions, and two-step procedures. Hence, the development of a one-step synthetic method using stable reagents under neutral conditions would be useful. Among the methods for the introduction of selenium moiety into organic molecules, the use of selenide anions is especially convenient and common. In general, the methods for the preparation of selenide anions include reductive cleavage of the Se-Se bond by various reducing agents such as $NaBH_4$,[6] $LiAlH_4$,[7] Na/NH_3,[8] Bu_3SnH,[9] SmI_2,[10] reaction of Grignard reagents with selenium,[11] and of selenols with sodium hydride or even with aqueous sodium hydroxide under certain conditions.[12]

Much attention has been paid to organometallic reactions in aqueous media in recent years.[13] The aqueous medium offers a powerful tool for minimizing waste production and harmful organic solvent dispersal.[14] Some particular properties of water make this solvent very attractive (i.e. non-toxicity, non-inflammability, high heat capacity, possibility of controlling pH and isolating insoluble solid products by filtration and recycling inorganic catalysts and water itself), allowing organic processes in aqueous medium to be safer, very efficient and highly selective.[15] Recently, transition metal selenolates or complexes have been widely used in synthesis of organoselenium compounds,[16-18] but reports exploring zinc selenolates are rare.[19] As a part of our interest in zinc chemistry,[19a-f] we are in constant search for novel applications of zinc selenolates in chemical reactions. Recently, an efficient one-pot route to unsymmetrical diorganyl selenides has been reported by ruthenium (III) chloride catalyzed reactions of dibenzyl or diphenyl diselenides with alkyl halides in the presence of zinc.[19g]

Among the useful and general methods for the preparation of selenoformates, we can cite those involving the reaction of phenylselenol with chloroformates in benzene and in the presence of pyridine,[2] treatment of phenylselenotris(trimethylsilyl)silane with chloroformates in the presence of tetrakis(triphenylphosphine)palladium (0),[20] the reaction of sodium phenylselenolate with chloroformates,[21] and water accelerated Sm/TMSCl reductive cleavage of the Se-Se bonds followed by subsequent reaction with methylchloroformate. Unfortunately, these methods suffer from serious drawbacks such as difficultly available reagents, laborious removal of by-products, such as diaryl diselenides, and tedious work-up procedures. Very recently, we reported a procedure for the preparation of selenoformates in 65-78% yields *via* a one-pot zinc-mediated reaction of diaryl diselenides and chloroformates in aqueous media;[23] this method required 1-1.5 hr for completion while the present procedure required less time (except for **3d** and **3f**). We now describe an improved method for the preparation of alkyl arylselenoformates from several diaryl diselenides and chloroformates by reductive cleavage of Se-Se bond promoted by the Zn/$RuCl_3$ system.

Simple stirring of diselenides **1** with metallic zinc dust in the presence of $RuCl_3$ (5 mol%) in CH_3CN-H_2O (5:1) mixed solvent at 70°C produced the zinc selenolate intermediate **2**. This was followed by addition of chloroformates which gave, after work-up, the desired product **3** with yields ranging from 86-97% (*Table*). As shown in the Table, a series of chloroformates (both aliphatic and aromatic) were treated with zinc arylselenolates in the presence of the Zn/$RuCl_3$ system; these reactions are in general rapid (15-90 min) and clean giving alkyl arylselenoformates in high to excellent yields.



$$\underset{1}{R^1Se{-}SeR^1} \xrightarrow[CH_3CN/H_2O,\ 70^\circ C]{Zn/RuCl_3} \underset{2}{[(R^1Se)_2Zn]} \xrightarrow{R^2OCOCl} \underset{3}{R^1SeCO_2R^2}$$

Scheme 1

In conclusion, the procedure described above is a simple and very efficient protocol for the synthesis of alkyl arylselenoformates. This method offers several significant advantages, such as simple reaction procedure, ready availability of the catalysts, neutral and mild reaction conditions, easy work-up, and high yields of the products and thus presents a good alternative to the existing procedures.[2,20-23]

EXPERIMENTAL SECTION

IR spectra were obtained using an ABB FTLA 2000 instrument. NMR spectra were recorded on a Bruker AQS 300 Avance instrument at 300 MHz for ^1H and at 75 MHz for ^{13}C NMR in $CDCl_3$ solutions.

General Procedure for the Synthesis of Alkyl Arylselenoformates.- A mixture of diselenide (0.5 mmol), zinc dust (2 mmol), and ruthenium (III) chloride hydrate (0.027 mmol) was suspended in CH_3CN (10 mL) and H_2O (2 mL). The mixture was stirred at 70°C for 1.5 h, during which time the zinc powder was almost completely consumed. Then, chloroformate (1.05 mmol) was added at once to the mixture and stirring was continued at that temperature for the appropriate time (*Table*). After completion of the reaction, the mixture was filtered, the filtrate was evaporated, and the residue was subjected to preparative TLC (silica gel, eluent, *n*-hexane-EtOAc = 10:1) to afford the pure selenoformate as yellow oil or white powder.

Table. Preparation of Selenoformates *via* Zinc Selenolate Anion Intermediate

Cmpd	R^1	R^2	Yield (%)[a,b]	Time (min)	mp./bp. (°C)	*lit.* mp./bp. (°C)
3a	Ph	CH_3	96[23]	20	Yellow oil	Oil
3b	Ph	Ph	97[23]	15	White powder 61-62	61
3c	Ph	$CH_3(CH_2)_6CH_2$	92[23]	30	Yellow oil	Oil
3d	Ph	$(CH_3)_2CHCH_2$	91[23]	60	Yellow oil	Oil
3e	Ph	$CH_3(CH_2)_2CH_2$	89[23]	25	Yellow oil	Oil
3f	4-ClC_6H_4	$(CH_3)_2CHCH_2$	90[23]	90	Yellow oil	Oil
3g	4-ClC_6H_4	Ph	89[23]	15	White powder 87-88	88
3h	4-ClC_6H_4	$CH_3(CH_2)_6CH_2$	86[23]	35	Yellow oil	Oil
3i	4-ClC_6H_4	CH_3	92[23]	30	Yellow oil	Oil
3j	4-ClC_6H_4	$CH_3(CH_2)_2CH_2$	87[23]	45	Yellow oil	Oil

a) Yields of pure isolated products characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy. b) References for known compounds.

Acknowledgements.- We thank the K. N. Toosi University of Technology Research Council and Iranian National Science Foundation (INSF, Grant No. 86063/21) for financial support.

REFERENCES

1. (a) H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979); (b) S. Patai and Z. Rappoport (eds.), *"The Chemistry of Organic Selenium and Tellurium Compounds"*, Vol. 1, John Wiley, Chichester, 1993.

2. M. D. Bachi and E. Bosch, *J. Org. Chem.*, **57**, 4696 (1992).

3. (a) A. Krief and L. Hevesi, " *Organoselenium Chemistry*", Vol. 1, Springer, Berlin, 1988; (b) A. Krief, In " *Comprehensive Organometallic Chemistry*", B. M. Trost (ed.), p.85, Pergamon, Oxford, 1991.

4. (a) A. Krief and M. Derock, *Tetrahedron Lett.*, **43**, 3083 (2002); (b) C. Paulmier, " *Selenium Reagents and Intermediates in Organic Synthesis*", Pergamon, Oxford, 1986.

5. (a) B. C. Ranu, T. Mandal and S. Samanta, *Org. Lett.* **5**, 1439 (2003); (b) T. Nishino, M. Okada, T. Kuroki, T. Watanabe, Y. Nishiyama and N. Sonoda, *J. Org. Chem.*, **67**, 8696 (2002); (c) X. Zhao, Z. Yu, S. Yan, S. Wu, R. Liu, W. He and L. Wang, *J. Org. Chem.*, **70**, 7338 (2005).

6. K. B. Sharpless and R. F. Laura, *J. Am. Chem. Soc.*, **95**, 2697 (1973).

7. H. Suzuki, M. Yoshinaga, K. Takaoka and Y. Hiroi, *Synthesis*, 497 (**1985**).

8. E. E. Aynsley, N. N. Greenwood and J. B. Leach, *Chem. Ind.* (London) 379 (**1966**).

9. D. Crich and D. Grant, *J. Org. Chem.*, **70**, 2384 (2005).

10. Y. Zhang, Y. Yu and R. Lin, *Synth. Commun.*, **23**, 189 (1993).

11. D. Liotta, U. Sunay, H. Santiesteban and W. Markiewicz, *J. Org. Chem.*, **46**, 2605 (1981).

12. F. Taboury, *Bull. Soc. Chim. Fr.*, **29**, 761 (1903).

13. (a) A. Lubineau, J. Auge and Y. Quéneau, *Synthesis*, 741 (**1994**); (b) C. J. Li, *Chem. Rev.*, **93**, 2023 (1993).

14. (a) P. Tundo and P. T. Anastas, In *"Green Chemistry: Challenging Perspectives"*, Oxford University Press, Oxford, 1999; (b) J. M. DeSimone, *Science*, **297**, 799 (2002).

15. C. J. Li and T. H. Chang, In " *Organic Reactions in Aqueous Media*", Wiley, New York, 1997.

16. P. Meunier, B. Gaotheron and A. Mazouz, *J. Chem. Soc., Chem. Commun.*, 424 (**1986**).

17. A. Osuka, N. Ohmasa and H. Suzuki, *Synthesis*, 857 (**1982**).

18. W. Bao and Y. Zhang, *Synth. Commun.*, **25**, 1825 (1995).

19. (a) B. Movassagh and F. Mirshojaei, *Monatsh. Chem.*, **134**, 831 (2003); (b) B. Movassagh and M. Shamsipoor, *Synlett*, 1316 (**2005**); (c) B. Movassagh and M. Shamsipoor, *Synlett*, 121 (**2005**); (d) B. Movassagh, M. Shamsipoor and M. Joshaghani, *J. Chem. Res. (S)*, 148 (**2004**); (e) B. Movassagh and A. Fazeli, *Z. Naturforsch.*, **61b**, 194 (2006); (f) B. Movassagh and A. Tatar, *Synlett*, 1954 (**2007**); (g) X. Zhao, Z. Yu, S. Yan, S. Wu, R. Liu, W. He and L. Wang, *J. Org. Chem.*, **70**, 7338 (2005).

20. C. H. Schiesser and M. A. Skidmore, *J. Chem. Soc. Perkin Trans. 1*, 2689 (**1997**).

21. M. A. Lucas and C. H. Schiesser, *J. Org. Chem.*, **61**, 5754 (1996).

22. L. Wang and Y. Zhang, *Synth. Commun.*, **29**, 3107 (1999).

23. B. Movassagh and A. Fazeli, *Monatsh. Chem.*, **138**, 863 (2007).

****

SYNTHESIS OF SUBSTITUTED AROMATIC COMPOUNDS USING BTC/DMF AS VILSMEIER REAGENT

Submitted by W. K. Su,* Z. C. Lu and X. X. Zhang
(10/26/09)

College of Pharmaceutical Sciences, Zhejiang University of Technology
Zhejiang Key Laboratory of Pharmaceutical Engineering
Hangzhou, 310014, P. R. CHINA
e-mail: suweike@zjut.edu.cn

The wide synthetic potential of the Vilsmeier reaction has been known for years and its utility for achieving different transformations has been amply demonstrated.[1] It has been reported that some aliphatic substances could be annulated to aromatic compounds by treatment of $POCl_3$/DMF as the Vilsmeier reagent, such as acyclic ketones,[2] cyclohexenones,[3] and α,β-epoxy ketones[4] and etc.[5] Generally, the traditional Vilsmeier-Haack reagent employs toxic reagents such as phosgene and phosphorus oxychloride.[6] Recently, the utilization of Vilsmeier salts derived from *bis*-(trichloromethyl) carbonate (triphosgene, BTC) and N,N-dimethylformamide (DMF) has been explored extensively.[7] In previous papers, we reported organic reactions involving by BTC/DMF as the Vilsmeier reagent.[8] In continuation of our studies on a variety of applications of BTC, we herein report a convenient method for the preparation of some substituted aromatic compounds using BTC/DMF as Vilsmeier reagent under mild conditions.

We initially investigated various conditions for the annulation of 3-benzoylpentane-2,4-dione with BTC/DMF to aromatic compound as the model reaction for the optimal conditions. The postulated mechanism indicates that the formation of the aromatic ring is quite complex with the generation of some by-products.[9] The reaction was monitored by TLC until the starting material was consumed. The residue was purified by flash chromatography on silica gel. The assignments of structure was confirmed by ^1H NMR, ^{13}C NMR, MS, IR and elemental analysis or comparison with literature data.[10] The results are shown in *Table 1*.