

## Synthesis, Characterization, and Crystal Structure of Hexavalent Bis (2-Pyridyl)/2-Pyridyl Aryl Selenones

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**ABSTRACT** Hexavalent oxide derivatives of *bis*(2-pyridyl)/2-pyridyl aryl selenides are anticipated as a new class of biological active compounds due to the presence of pyridine ring, that act as essential building blocks for numerous biological functions. Thus, the development of new methodologies for the synthesis of this class of compounds represents a prime endeavor in synthetic chemistry. A variety of 2-pyridyl aryl selenones has, therefore, been synthesized through N-protected oxidation of corresponding 2-pyridyl aryl selenides. Oxidation of the prepared selenides was carried out using potassium permanganate, a powerful oxidizing agent in glacial acetic acid as solvent by stirring at room temperature. The completion of the reaction was confirmed with the chromatographic method such as thin layer chromatography. The reaction mixture was neutralized with saturated solution of sodium bicarbonate and extracted with dichloromethane, which on evaporation of solvent and recrystallization resulted into the synthesis of titled white crystalline solid *bis*(2-pyridyl)/2-pyridyl aryl selenones. All these newly synthesized unknown selenones were characterized analytically, thermo gravimetrically analysis, and through nuclear magnetic resonance, infrared, mass spectrometry, and crystallography. X-ray crystal analysis of *bis*(2-pyridyl)/2-(3-methylpyridyl) phenyl selenones was performed which reveals the monoclinic structure with P21/c for 2-(3-methylpyridyl) phenyl selenone whereas triclinic with P-1 space group for *bis*(2-pyridyl) selenone.

**KEYWORDS** 2-Pyridyl, Glacial acetic acid, Phenyl, Potassium permanganate, Selenone.

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### INTRODUCTION

Organoselenium chemistry is making headways in diverse areas ranging from organic synthesis<sup>[1]</sup> to coordination chemistry<sup>[2]</sup> and material sciences.<sup>[3]</sup> The versatility of reactants and reagents based on elemental selenium has led to the rapid development in chemistry of organoselenium compounds.<sup>[4,5]</sup> In the present studies, many of the transformations revolve around the oxidation of bivalent selenides to the corresponding monoxide intermediates, that

is, tetravalent selenoxide. These selenoxides have been used as intermediates in facile eliminations,<sup>[6]</sup> proceed with *syn* stereospecificity,<sup>[7]</sup> in Purmmerer- type<sup>[8]</sup> and Sigmatropic rearrangements,<sup>[9]</sup> for the preparation of chiral alcohol,<sup>[10]</sup> in catalytic green chemistry.<sup>[11]</sup>

Compared to the well documented chemistry of tetravalent selenoxides, hexavalent oxide derivatives of aryl/alkyl selenides have received much less attention and there is no convenient method for their preparation.<sup>[12]</sup> Preparation of selenones is known to require highly vigorous conditions.<sup>[11]</sup>

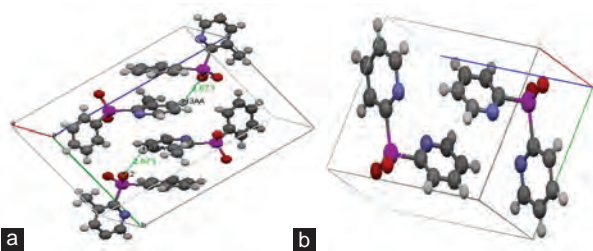
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**Figure 3:** Cubic crystal packing of (a) 2-(3-methylpyridyl) phenyl selenone (b) bis(2-pyridyl) selenone with O...H intermolecular interactions

obtained by dissolving small amount of compounds individually in minimum quantity of solvent mixture of chloroform and carbon-tetrachloride (1:1, v/v) by slow evaporation of solvent at room temperature. Suitable, with well-defined shape, crystal of both above mentioned selenones was chosen from crop of crystals and mounted on glass fiber separately. Data sets were collected for cell determination and intensity data collection. The structures were resolved by direct methods and refined by full-matrix least squares method using SHELX-97 (Sheldrick 2008) program package. All hydrogen atoms were included in the refinement at geometrically ideal positions and refined with a riding model. The MERCURY package and the ORTEP for Windows program were used for generating the structures.

### Synthesis of bis(2-pyridyl)/2-pyridyl aryl selenones

1.0 mmoles of bis(2-pyridyl)/2-pyridyl aryl selenides was taken in 10.0 mL of glacial acetic acid and potassium permanganate (0.55 g, 3.5 mmol) was added to the above solution in small portions with stirring that was carried out at room temperature and the completion of the reaction was confirmed by TLC. Once the reaction was complete, the reaction mixture was neutralized with excess of saturated solution of sodium bicarbonate and extracted with dichloromethane (4 × 25 mL). The organic layer was washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to afford corresponding selenones which were recrystallized from solvent mixture of chloroform and carbon tetrachloride (1:1, v/v) to yield pure fine crystals of selenones in excellent yields [Scheme 1].

### CONCLUSIONS

We have reported a one pot general, convenient, and economical methodology for the synthesis of bis(2-pyridyl)/2-pyridyl aryl selenones through oxidation of corresponding selenides with potassium permanganate in glacial acetic acid. The structures of all the newly synthesized selenones have been elucidated using elemental analysis,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{77}\text{Se}$  NMR spectroscopy, IR, and mass spectrometry in conjunction with single-crystal X-ray crystallography.

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### REFERENCES

- [1] a) Clive, D.L. Modern organoselenium chemistry, *Tetrahedron*, **1978**, *34*, 1049–1132; b) Procter, D.J. The synthesis of thiols, selenols, sulfides, selenides, sulfoxides, selenoxides, sulfones and selenones, *J. Chem. Soc. Perkin Trans. 1*, **2000**, *6*, 835–871; c) Beletskaya, I.P., Ananikov, V.P., Transition-metal-catalyzed C-S, C-Se, and C-Te bond formation via cross-coupling and atom-economic addition reactions, *Chem. Rev.*, **2011**, *111*, 1596–1636.
- [2] Kumbhare, L.B., Wadawale, A., Zade, S.S., Jain, V.K. Oligomeric allyl-palladium (ii) complexes of  $\beta$ -substituted ethylselenolates: Syntheses, structures and thermal decomposition, *Dalton Trans.*, **2011**, *40*, 7957–7966.
- [3] Sharma, R.K., Kedarnath, G., Jain, V.K., Wadawale, A., Pillai, C.G.S., Nalliath, M., Vishwanadh, B. Copper (I) 2-pyridyl selenolates and tellurolates: Synthesis, structures and their utility as molecular precursors for the preparation of copper chalcogenide nanocrystals and thin films, *Dalton Trans.*, **2011**, *40*, 9194–9201.
- [4] Back, T.G., editor. *Organoselenium Chemistry, a Practical Approach*, Oxford University Press, Oxford, **1999**; b) Krief A. In: Abel, E.W., Stone, F.G.A., Wilkinson, G., editors. *Comprehensive Organometallic Chemistry II*, Vol. 2. Pergamon, New York, **1995**, p515–569.
- [5] a) Reich, H.J. *Oxidation in Organic Chemistry*, Vol. 5. Elsevier, Amsterdam, Netherlands, **1978**, p1–130; b) Reich H.J. Functional group manipulation using organoselenium reagents, *Acc. Chem. Res.*, **1978**, *11*, 22; c) Back, T.G. *Encyclopedia of Inorganic Chemistry*, Wiley, New York, **2006**.
- [6] a) Reich, H.J. Functional group manipulation using organoselenium reagents, *Acc. Chem. Res.*, **1979**, *12*, 22–30; b) Liotta, D. New organoselenium methodology, *Acc. Chem. Res.*, **1984**, *17*, 28; b) Sharpless, K.B., Laurer, R.F. Mild procedure for the conversion of epoxides to allylic alcohols. First organoselenium reagent, *J. Am. Chem. Soc.*, **1973**, *95*, 2697–2699; c) Sharpless, K.B., Laurer, R.F., Teranishi, A.Y. Electrophilic and nucleophilic organoselenium reagents. New routes to  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds, *J. Am. Chem. Soc.*, **1973**, *95*, 6137–6139.
- [7] Sharpless, K.B., Young, M.W., Lauer, R.F. Reactions of selenoxides: Thermal syn-elimination and  $\text{H}_2^{18}\text{O}$  exchange, *Tetrahedron Lett.*, **1973**, *14*, 1979–1982.
- [8] Galambos, G., Simonidesz, V. A pummerer-type rearrangement of selenides, *Tetrahedron Lett.*, **1982**, *23*, 4371–4372.
- [9] a) Reich, H.J., Wollowitz, S. Conversion of allyl alcohols to 1, 3-dienes by sequential sulfenate sulfoxide [2, 3]-sigmatropic rearrangement and syn-elimination, *J. Am. Chem. Soc.*, **1982**, *104*, 7051–7059;



- b) Reich, H.J., Yelm, K.E., Wollowitz, S. Kinetics, thermodynamics and stereochemistry of the allyl sulfoxide-sulfenate and selenoxide-selenenate [2,3] sigmatropic rearrangements, *J. Am. Chem. Soc.*, **1983**, *105*, 2503–2504.
- [10] Komatsu, N., Nishibayashi, Y., Uemura, S. Asymmetric [2, 3] sigmatropic rearrangement via chiral selenoxide with sharpless oxidants, *Tetrahedron Lett.*, **1993**, *34*, 2339–2342.
- [11] Freudendahl, D.M., Santoro, S., Shahzad, S.A., Santi, C., Wirth, T. Grüne chemie mit selenreagentien: Entwicklung effizienter katalytischer reaktionen, *Angew. Chem.*, **2009**, *121*, 8559–8562.
- [12] Nishibayashi, Y., Singh, J.D., Fukuzawa, S., Uemura, S. Synthesis of [R, S, R, S]-and [S, R, S, R]-Bis [2-[1-(dimethylamino) ethyl] ferrocenyl] diselenides and their application to asymmetric selenoxide elimination and [2, 3] sigmatropic rearrangement, *J. Org. Chem.*, **1995**, *60*, 4114–4120.
- [13] Irgolic, K.J. *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, **1978**.
- [14] Nakayama, J. 1-Oxides and 1, 1-dioxides of thiophenes and selenophenes and related compounds, *Bull Chem. Soc. Jpn.*, **2000**, *73*, 1–17.
- [15] Wheelock, C.E., Colvin, M.E., Uemura, I., Olmstead, M.M., Sanborn, J.R., Nakagawa, Y., Jones, A.D., Hammock, B.D. Use of ab initio calculations to predict the biological potency of carboxylesterase inhibitors, *J. Med. Chem.*, **2002**, *45*, 5576–5593.
- [16] Mousa, S.A., Connor, L. O., Rossman, T.G., Block, E. Pro-angiogenesis action of arsenic and its reversal by selenium-derived compounds *Carcinogenesis*, **2007**, *28*, 962–967.
- [17] Toshimitsu, A., Uemura, S. In: Back, TG, editor. *Organoselenium Chemistry: A Practical Approach*, Oxford University Press, Oxford, **1999**, p241.
- [18] Irgolic, K.J. Tellurium literature survey covering the year 1976, *J. Organomet. Chem.*, **1978**, *158*, 235–266.
- [19] Wirth, T. In: Crabtree, R.H., Mingos D.M., editors. *Comprehensive Organometallic Chemistry III*, Vol. 9. Elsevier, Oxford, **2006**, p457-499.
- [20] Reich, H.J. Berry, E.J., McWhinnie, W.R., editors. *Proceedings of the 4<sup>th</sup> International Symposium on Organic Selenium and Tellurium Compounds*, Birmingham, UK, **1983**, p268.
- [21] a) Wirth, T., editor. *Organoselenium Chemistry: Modern Developments in Organic Synthesis*, Vol. 208. Springer, Berlin, **2000**; b) Back, T.G., editor. *Organoselenium Chemistry: A Practical Approach*, Oxford, New York: Oxford University Press, **2000**.
- [22] Bagnoli, L., Scarponi, C., Testaferri, L., Tiecco, M. Preparation of both enantiomers of cyclopropane derivatives from the reaction of vinyl selenones with di-(–)-bornyl malonate, *Tetrahedron Asymmetry*, **2009**, *20*, 1506.
- [23] a) Tripathi, S.K., Sharma, S., Singh, H.B., Butcher, R.J. 2-Phenoxyethanol derived diselenide and related compounds, synthesis of a seven-membered seleninate ester, *Org. Biomol. Chem.*, **2011**, *9*, 581–587.
- [24] Khurana, J.M., Kandpal, B.M., Chauhan, Y.K. Rapid oxidation of selenides, selenoxides, tellurides, and telluroxides with aqueous sodium hypochlorite, *Phosphorus Sulfur Silicon*, **2003**, *178*, 1369–1375.
- [25] Jones, D.N., Mundy, D., Whitehouse, R.D. Selenium and tellurium chemistry, *J. Chem. Soc. Chem. Commun.*, **1970**, *4*, 86–87.
- [26] Oba, M., Okada, Y., Endo, M, Tanaka, K., Nishiyama, K., Shimada S., Ando, W. Formation of diaryl telluroxides and tellurones by photosensitized oxygenation of diaryl tellurides, *Inorg. Chem.*, **2010**, *49*, 10680–10686.
- [27] Makarov, A.G., Makarov, A.Y., Bagryanskaya, I.V., Shakirov, M.M., Zibarev, A.V. New polyfluorinated aromatic and aza-aromatic diselenides, selenyl chlorides, non-symmetric selenides and selenoxides, *J. Fluorine Chem.*, **2012**, *144*, 118–123.
- [28] Gujral, G., Bhasin, K.K., Gulati, S. A new synthetic methodology for the preparation 2-pyridyl anisyl/benzyl selenides: A X-ray crystal structure of 2-(4-methyl pyridyl) tolyl selenide. *Indian J. Heterocycl. Chem.*, **2021**, *31*, 497–503.
- [29] Bhasin, K.K., Doomra, S., Kaur, G., Arora, E., Singh, N., Nagpal, Y., Kumar, R., Rishu, Klapotke, T.M., Mehta, S.K. Synthesis of unsymmetrical pyridyl aryl selenides by the reductive cleavage of Se-Se bond, *Phosphorus Sulfur Silicon Relat. Elem.*, **2008**, *183*, 992–997.
- [30] Oszczapowicz, J. Substituent effects in the <sup>13</sup>C-NMR spectra of six-membered nitrogen heteroaromatic compounds, *Int. J. Mol. Sci.*, **2005**, *6*, 11.

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