

Design, Synthesis, Characterization, and Crystal Structures of 2-Pyridyl Naphthyl Selenides

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ABSTRACT A convenient method for the preparation of several unsymmetrical 2-pyridyl/4-aryl 1-naphthyl selenides is presented. The newly prepared compounds have been obtained in good yields by the reaction of substituted 2, 2'-dipyridyl diselenides with 1-bromo naphthalene or vice-versa using cuprous oxide-bipyridyl catalyst employing magnesium as reductant in dimethyl formamide. A combination of both the copper catalyst and magnesium proved ideal to afford the title compounds in good results. The newly synthesized 2-pyridyl/4-aryl 1-naphthyl selenides are either viscous liquids or crystalline solids that are stable at room temperature for several months without decomposition. The compounds were fully characterized by various spectroscopic techniques, namely, NMR (¹H, ¹³C, ⁷⁷Se), IR, and mass spectroscopy. Single crystal X-ray diffraction study was carried out on four molecules to know unambiguously their structural details. Well-defined diffraction quality crystals were obtained by dissolving the compounds in dichloromethane and then layering with hexane followed by slow evaporation.

KEYWORDS Selenide, Pyridyl, Naphthyl, Phenyl, Tollyl, Reductive cleavage

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INTRODUCTION

Selenium, an ubiquitous metalloid and a third member of the chalcogen group, is currently being considered as a unique essential micronutrient^[1] and a fundamental element in biological systems.^[2] It replaces sulfur in cysteine and forms the 21st amino acid called selenocysteine. Interesting potential biological properties, namely, antioxidant, antihypertensive, and anticancer exhibited by selenium containing compounds^[3] in living beings have been proved to be highly valuable in organic chemistry over the past four decades. Organoselenium compounds, especially those containing nitrogen atoms, are attractive molecules because of their key role in organic synthesis.^[4] Consequently, the development of efficient methodologies for the synthesis of nitrogen functionalized organochalcogen compounds is of

vital significance in the field of chemical research. Pyridine constitutes an important motif in heterocyclic compounds in the context of nitrogen-functionalized compounds as pyridine derivatives have numerous applications in the realm of bioactive molecules. Consequently, a galaxy of methods for the preparation of diorganyl selenides/diorganyl diselenide has been well documented^[5] during the past few years. Despite the advantages coupled with increasing applicability of organoselenium compounds, current synthetic methods have been limited in use by lengthy synthetic steps, hazardous solvents, harsh reaction conditions, unstable intermediates, and a limited diversity of functional groups of starting materials.

Aryl carbon-chalcogen bond formation is one of the fundamental reactions in organic synthesis and transition-metal-catalyzed C-Se bond formation attests the most popular

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- [2] Weekley, C.M., Aitken, J.B., Finney, L., Vogt, S., Witting, P.K., Harris, H.H. Selenium metabolism in cancer cells: The combined application of XAS and XFM techniques to the problem of selenium speciation in biological systems, *Nutrients*, **2013**, 5, 1734–1756.
- [3] (a) Steinbrenner, H., Sies, H. Selenium homeostasis and antioxidant selenoproteins in brain: Implications for disorders in the central nervous system, *Arch. Biochem. Biophys.*, **2013**, 536, 152–157; (b) Zhao, L., Li, J., Li, Y., Liu, J., Wirth, T., Li, Z. STAT6 phosphorylation inhibitors block eotaxin-3 secretion in bronchial epithelial cells, *Bioorg. Med. Chem.*, **2012**, 20, 750–758; (c) Nogueira, C.W., Barbosa, N.V., Rocha, J.B.T. Toxicology and pharmacology of synthetic organoselenium compounds: An update, *Arch. Toxicol.*, **2021**, 95, 1179–1226.
- [4] (a) Rathore, V., Jose, C., Kumar, S. Organoselenium small molecules as catalysts for the oxidative functionalization of organic molecules, *New J. Chem.*, **2019**, 43, 8852–8864; (b) Sperança, A., Godoi, B., Zeni, G. Iron(III) chloride/diorganyl diselenides: A tool for intramolecular cyclization of alkynone O-methyloximes, *J. Org. Chem.*, **2013**, 78, 1630–1637.
- [5] (a) Bonaterrea, M., Martín, S.E., Rossi, R.A. Palladium-catalyzed phenyl-selenylation with n-Bu₃SnSePh in one-pot two-step reactions, *Tetrahedron Lett.*, **2006**, 47, 3511–3515; (b) Cohen, R.J., Fox, D.L., Salvatore, R.N. A novel and highly efficient synthetic route to unsymmetrical organoselenides using cesium bases, *J. Org. Chem.*, **2004**, 69, 4265–4268; (c) Nishino, T., Okada, M., Kuroki, T., Watanabe, T., Nishiyama, Y., Sonoda, N. One-pot synthetic method of unsymmetrical diorganyl selenides: Reaction of diphenyl diselenide with alkyl halides in the presence of lanthanum metal, *J. Org. Chem.*, **2002**, 67, 8696–8698.
- [6] (a) Ajiki, K., Hirano, M., Tanaka, K. Rhodium-catalyzed reductive coupling of disulfides and diselenides with alkyl halides, using hydrogen as a reducing agent, *Org. Lett.*, **2005**, 7, 4193–4195; (b) 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.
- [7] Qiao, Z., Liu, H., Xiao, X., Fu, Y., Wei, J., Li, Y., Jiang, X. Efficient access to 1,4-benzothiazine: Palladium-catalyzed double C-S bond formation using Na₂S₂O₃ as sulfuring reagent, *Org. Lett.*, **2013**, 15, 2594–2597.
- [8] Zhang, C.P., Vicic, D.A. Nickel-catalyzed synthesis of aryl trifluoromethyl sulfides at room temperature. *J. Am. Chem. Soc.*, **2012**, 134, 183–185.
- [9] Ranu, B.C., Dey, R., Chatterjee, T., Ahammed, S. Copper nanoparticle-catalyzed carbon-carbon and carbon-heteroatom bond formation with a greener perspective, *ChemSusChem*, **2012**, 5, 22–44.
- [10] Ranu, B.C., Saha, A., Mandal, T. An indium-TMSCl promoted reaction of diphenyl diselenide and diorganyl disulfides with aldehydes: Novel routes to selenoacetals, thioacetals and alkyl phenyl selenides, *Tetrahedron*, **2009**, 65, 2072–2074.
- [11] Kassaee, M.Z., Motamedi, E., Movassagh, B., Poursadeghi, S. FeNPs-catalyzed C-Se and C-Te bond formation reactions, *Synthesis*, **2013**, 45, 2337–2342.
- [12] Eichman, C.C., Stambuli, J.P. Transition metal catalyzed synthesis of aryl sulfides. *Molecules* **2011**, 16, 590–608.
- [13] Ibrahim, M., Hassan, W., Meinerz, D.F., dos Santos, M., Klimaczewski, C.V., Deobald, A.M., Costa, M.S., Nogueira, C.W., Barbosa, N.B.V., Rocha, J.B.T. Antioxidant properties of diorganoyl diselenides and ditellurides: Modulation by organic aryl or naphthyl moiety, *Mol. Cell. Biochem.*, **2012**, 97, 371–372.
- [14] Luchese, C., Brandão, R., Acker, C.I., Nogueira, C.W. 2, 2'-Dipyridyl diselenide is a better antioxidant than other disubstituted diaryl diselenides, *Mol Cell Biochem* **2012**, 367, 153-163; a) 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; b) Bhasin, K.K., Doomra, S., Kaur, G., Arora, E., Singh, N., Nagpal, Y., Kumar, R., Rishu, Klapoetke, 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.
- [15] (a) Bhasin, K.K., Gupta, V., Gupta, S.K., Sanan, K., Sharma, R.P. Synthesis and characterisation of alkyl-1-naphthyl selenides and tellurides, *Ind. J. Chem.*, **1994**, 33A, 1110–1112; (b) Bhasin, K.K., Singh, J. A novel and convenient synthesis towards 2-pyridylselenium compounds: X-ray crystal structure of 4,4'-dimethyl-2,2'-dipyridyl diselenide and tris(2-pyridylseleno) methane, *J. Organomet. Chem.*, **2002**, 658, 71–76.
- [16] Nakanishi, W., Hayashi, S., Uehara, T. Structure of 1-(arylselanyl)naphthalenes-Y dependence in 1-(p-YC₆H₄)Se C₁₀H₇, *Eur. J. Org. Chem.*, **2001**, 20, 3933–3943.
- [17] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed. Ithaca Cornell University Press, New York, **1960**, p244.
- [18] Bhasin, K.K., Singh, N., Dhiman, R., Ram, G., Shivani, Mehta, S.K., Butcher R.J. Synthesis and characterization of some α -naphthyl selenium/tellurium derivatives: X-ray crystal structure of benzyl-1-naphthyl selenide and diphenylmethyl-1-naphthyl selenide, *J. Organomet. Chem.*, **2006**, 691, 621–628.
- [19] Sheldrick, G.M. A short history of SHELX, *Acta Cryst.*, **2008**, A64, 112–122.
- [20] (a) Macrae, C.F., Bruno, I.J., Chisholm J.A., Edgington, P.R., McCabe, P., Pidcock, E., Monge, L.R., Taylor, R., van de Streek, J., Wood, P.A. Mercury CSD 2.0-new features for the visualization and investigation of crystal structures, *J. Appl. Cryst.*, **2008**, 41, 466–470; (b) Farrugia, L.J. WinGX and ORTEP for windows: An update. *J. Appl. Cryst.*, **2012**, 45, 849–854.
- [21] Singh, J. Design, Synthesis and Characterisation of 2-picolyl and Methyl Substituted 2-Pyridyl Chalcogen (Se, Te) Compounds and their Derivatives, Ph.D. Thesis, Panjab University, Chandigarh, **2003**.