SYNLETT
Spotlight 463

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Potassium Selenocyanate

Compiled by Adrián A. Heredia

Adrián A. Heredia was born in 1988 in Córdoba, Argentina. He obtained his chemistry degree from the Facultad de Ciencias Químicas at the Universidad Nacional de Córdoba in 2011. Currently, he is working toward his Ph.D. under the supervision of Professor Alicia B. Peñéñory. His research interests focus on the developed of new synthetic strategies for the formation of C–S and C–Se bonds.

INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Haya de la Torre y Medina Allende, Ciudad Universitaria, X5000HUA Córdoba, Argentina
E-mail: aheredia@fcq.unc.edu.ar

Introduction

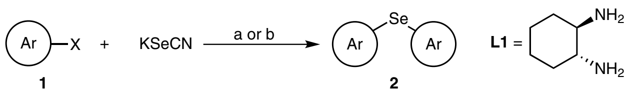
Potassium selenocyanate (KSeCN) is an easy-to-handle and readily available reagent. It is crystalline, colorless, highly hygroscopic, and air sensitive. Non-adequate storage may lead to its decomposition. This salt is soluble in protic solvents and non-protic polar solvent such as DMF, DMSO, NMP, and acetonitrile.

This reagent is commercially available and seldom prepared in the laboratory. It can be synthesized from metallic selenium and potassium cyanide in hot water or ethanol.

Methodologies employing KSeCN as the selenium source in the synthesis of organic selenocyanates and isoselenocyanates are practical and versatile. Because this functional group has a moderate reactivity, its conversion into other functional groups is highly interesting, allowing the formation of new C–Se bonds and the further generation of compounds with significant synthetic,[1] pharmacological, and biological value.[2]

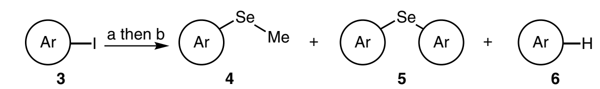
Abstracts

(A) KSeCN is used as an effective source of selenium in the synthesis of symmetrical diaryl selenides **2**. For example, Nageswar and co-workers have developed a methodology for the synthesis of **2** with aryl halides **1** catalyzed by recyclable CuO nanoparticles under ligand-free conditions in DMSO, using KOH as the base (conditions a).[3] Rao and co-workers reported the synthesis of **2** by copper-catalyzed cascade reactions with **1** and CuI–*trans*-1,2-diaminocyclohexane (**L1**) complex in water and using Cs_2CO_3 as the base (conditions b).[4] Under both conditions, a variety of aryl halides reacted with KSeCN to give the corresponding products in high yield.



X = Br, I
Ar = aryl, heteroaryl, vinyl
(a) nano-CuO (5 mol%), DMSO, 15 h, 110 °C (59–96%);
(b) CuI (10 mol%), **L1** (10 mol%), H_2O, Cs_2CO_3, 40 h, 100 °C (59–61%)

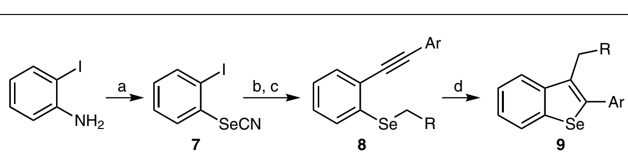
(B) Bouchet, Peñéñory and Argüello synthesized aryl methyl selenides **4** and diaryl selenides **5** employing KSeCN and aryl iodides **3** using base-assisted photoinduced electron-transfer reactions.[5] Aryl selenolate anions can be formed in the presence of *t*-BuOK as an *entrainment* reagent. Then, it can react with MeI or **3** yielding **4** or **5**, respectively. In this work, the authors undertook a comparative study of a set of selenium sources.



Ar =	4	5	6
1-Naph	67%	27%	7%
4-MeOC$_6$H$_4$	66%	21%	11%
2-MeC$_6$H$_4$	55%	10%	–
4-O$_2$NC$_6$H$_4$	75%	–	–

(a) KSeCN, *hν*, *t*-BuOK, DMSO, N_2, 3 h; (b) MeI

(C) It is well known that the selenocyanate anion can be introduced into arenes by diazonium salt formation, followed by nucleophilic displacement. Nakamura and co-workers, used this methodology to obtain 1-iodo-2-selenocyanatebenzene (**7**) as an intermediate to generate alkyl *ortho*-alkynylphenyl selenides **8** which cyclize in the presence of platinum, rendering 2,3-disubstituted benzo[*b*]selenophenes **9**.[6] That cyclization proceeds by carboselenation through the addition of a C–Se bond to the alkyne, followed by a direct 1,3-migration of the CH_2R group.



(a) HCl, $NaNO_2$, NaOAc, KSeCN; (b) KEt_3BH, RCH_2Cl;
(c) $PdCl_2$, CuI, arylacetylene, DIPEA;
(d) $PtCl_2$ (5 mol%), toluene, 25 °C, 1 h (77–100%)

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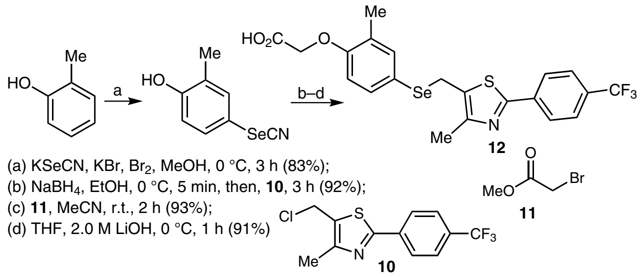
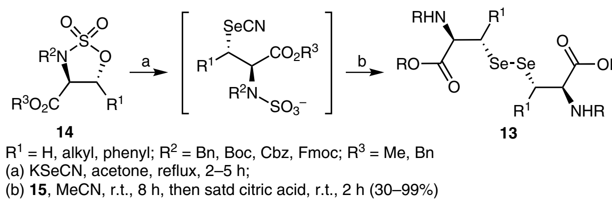
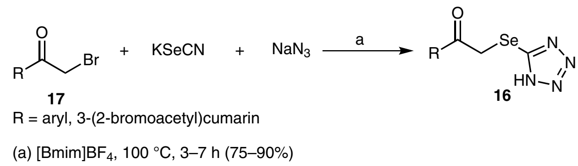
(D) In the presence of an oxidizer, such as Br_2, KSeCN forms $(SeCN)_2$, which plays the role of the electrophile in electrophilic aromatic substitution reactions. This methodology was used by Sharma et al. for the synthesis of thiazole **12**. This compound is a powerful PPARβ/δ ligand which may possess anti-cancer properties.[7]



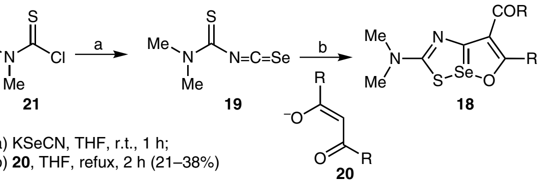
(E) Chandrasekaran and co-workers have developed a protocol for the synthesis of *N*-alkyl-β-aminodiselenides **13** from sulfonamidates **14** in the presence of KSeCN and benzyltriethylammonium tetrathiomolybdate ($[BnEt_3N]MoS_4$, **15**) in a one-pot reaction.[8] This methodology has been successfully applied in the synthesis of selenocystine derivatives and their direct incorporation into peptides.



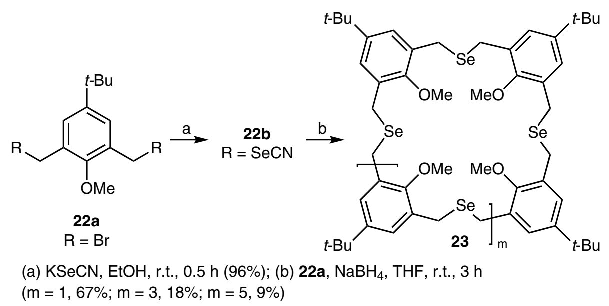
(F) The C≡N triple bond of organic selenocyanates can react with sodium azide to form selenium-substituted tetrazoles.[9] Chandramouli and co-workers proposed a simple and convenient method for the synthesis of selenyl tetrazoles **16** by a one-pot three-component reaction between phenacyl bromides or 3-(2-bromoacetyl)coumarins **17**, KSeCN, and sodium azide in ionic liquids.



(G) KSeCN reacts with acid chlorides or their analogues, thus obtaining isoselenocyanates. Ishihara and co-workers were able to synthesize 1-thia-6-oxa-6aλ^4-seleno-3-azapentalene (**18**) from thiocarbamoyl isoselenocyanate **19** and β-diketone-derived anions **20**. Compound **19** was obtained by reaction of KSeCN with dimethylcarbamothioic chloride (**21**).[10]



(H) Dehaen and co-workers employed KSeCN and 1,3-bis(bromomethyl)benzene derivates **22a** for the synthesis of homoselenocalix[*n*]arenes (**23**, $n = 4$, 6 and 8).[11a] In a later publication, they synthesized other analogues of **23** and demonstrated the coordination ability of those supramolecular structures to silver(I) ion through the selenium atoms.[11b]



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