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Green Synthetic Approaches For Organo Chalcogens [Te & Se]

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Abstract: Organochalcogen compounds, particularly those containing selenium (Se) and tellurium (Te), exhibit unique redox, electronic, and biological properties, making them highly relevant in medicinal chemistry, catalysis, and advanced materials. Traditional synthesis of these frameworks often involves hazardous solvents, stoichiometric reagents, and energy-intensive conditions that conflict with sustainable practices. This work explores **green synthetic methodologies** for organochalcogen compounds with a focus on atom economy, waste minimization, and environmentally benign conditions.

We emphasize microwave-assisted reactions, solvent-free mechanochemistry, and ultrasonic techniques as effective pathways to heterocycles, chalcogen-bridged scaffolds, and seleno- and telluroethers. Furthermore, safer and recyclable substitutes for conventional organic solvents are offered by the use of aqueous media, ionic liquids, and deep eutectic solvents. These techniques greatly lessen environmental impact without sacrificing product functionality, according to a comparative analysis of yields, E-factor, and energy profiles. Preliminary biological and optoelectronic tests verified a few molecules, demonstrating performance on par with or better than that of traditionally produced equivalents. All things considered, this study highlights how green synthetic methods can successfully combine sustainability and creativity in organochalcogen chemistry, opening up new possibilities for environmentally friendly research and industrial uses.

Keywords: Green chemistry, Organochalcogen, Microwave-assisted reactions.

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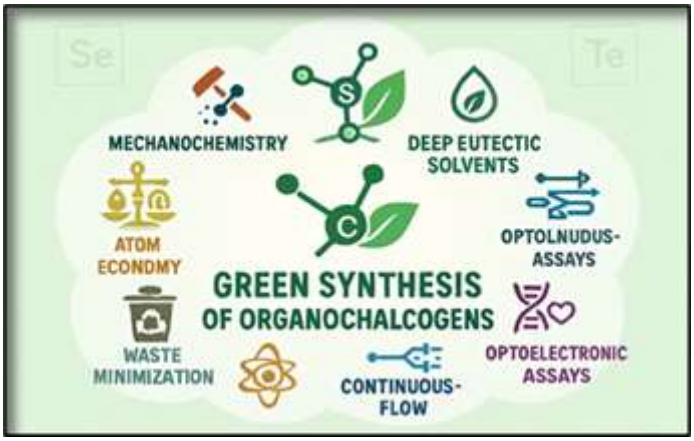
Graphical Abstract:



1. Introduction

Because of their special redox characteristics and their functions as adaptable intermediates in the synthesis of complex natural products, organoselenium and organotellurium compounds are essential in synthetic organic chemistry. While synthetic organotellurides have demonstrated potential as strong antioxidants and antibacterial agents, selenium is an essential element found in selenoproteins (such as glutathione peroxidase) in biological situations.

However, the "classic" synthesis of these compounds frequently uses poisonous, foul-smelling reagents, such as hydrogen selenide (H_2Se), or stoichiometric quantities of metallic reductants in chlorinated solvents**[1]**. Current research aims to minimize the E-factor (Environmental factor) by using safer solvent systems (water, PEG, or solvent-free circumstances) and alternative energy sources (microwave, ultrasound, mechanical energy) in accordance with the 12 Principles of Green Chemistry. This study assesses the transition to these sustainable approaches, emphasizing their quantitative sustainability and mechanistic benefits.

2. Methodology

This study compares documented green practices to conventional standards using a comparative analytical framework. The two main chalcogens, tellurium and selenium, are the center of the methodology, which classifies their synthesis according to the green activation technique used.

The methodological framework of this study is dependent on the strategic activation of chalcogen-chalcogen (E-E, where E = Se, Te) and chalcogen-halide bonds through non-thermal energy transfer. Our method emphasizes organized molecular interactions on solid-

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phase surfaces [2].In contrast to conventional techniques that rely on stochastic thermal collisions in a refluxing organic liquid. We take advantage of the large surface-area-to-volume ratio of the solid support to enable quick nucleophilic or electrophilic attack by using heterogeneous catalysts like KF/Al2O3 and silica-supported reagents. In microwave-assisted methods, dielectric heating further increases this interfacial reactivity by producing localized energetic gradients due to the catalyst surface's differential polarization, which considerably reduces the activation energy barrier in comparison to isotropic heating.

Additionally, the inherent solubility issues of organochalcogen precursors are addressed by the combination of micellar aqueous medium and Mechanochemical Liquid-Assisted Grinding (LAG) [3]. The methodology uses a "bottom-up" sustainability assessment in which each reaction's efficiency is measured using Atom Economy (AE) and Reaction Mass Efficiency (RME) in addition to chemical yield. By employing in situ produced nucleophiles (e.g., tellurolates or selenolates) in aqueous or solvent-free conditions, we minimize the necessity for the isolation of unstable and hazardous intermediates [4]. The synthesized C-Se and C-Te designs preserve strong regio- and stereo-selectivity while meeting strict environmental benchmarks thanks to this simultaneous focus on kinetic acceleration and waste minimization.

3. Green Synthetic Methodology for OrganoSelenium (Se)

3.1. Mechanochemical Synthesis of Diselenides

Mechanochemistry offers a powerful alternative to traditional heating, utilizing mechanical force to initiate chemical transformations in the solid state. Chen, S., Fan, C., Xu, Z. et al. [5] very recently reported the mechanochemical synthesis of organoselenium compounds under mild conditions. The study includes the formation of magnesium-based selenium nucleophiles *in situ* from easily available organic halides, magnesium metal, and elemental selenium via mechanical stimulation. This process occurs under liquid-assisted grinding (LAG) conditions, requires no complicated pre-activation procedures, and operates broadly across a diverse range of aryl, heteroaryl, and alkyl substrates. In this work, symmetrical diselenides are efficiently obtained after work-up in the air, while one-pot nucleophilic addition reactions with various electrophiles allow the comprehensive synthesis of unsymmetrical monoselenides with high functional group tolerance. Notably, the method is applied to regioselective selenylation reactions of diiodoarenes and polyaromatic aryl halides that are difficult to operate via solution

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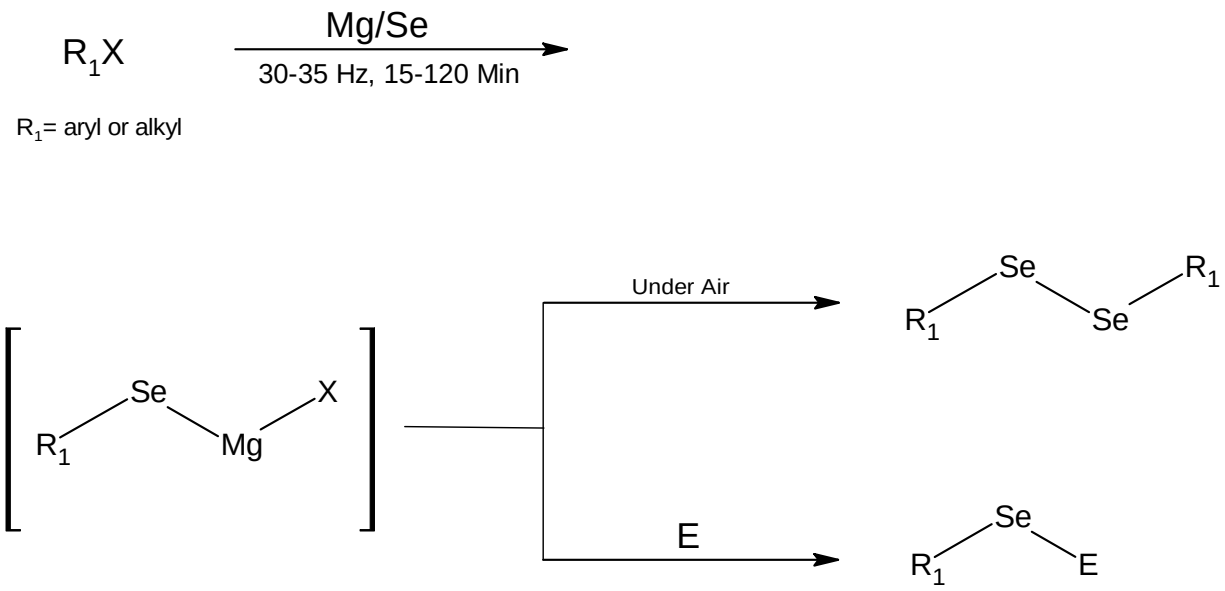
approaches. Besides selenium, elemental sulfur and tellurium are also competent in this process, which showcases the potential of the methodology for the facile synthesis of organochalcogen compounds. Very recently mechanochemical synthesis of organoselenium compounds.

Scheme 1:



Green Aspects:

- Excellence atom & step economy
- Green and sustainable chemistry concept
- The special mechnochemical C-Se bond formation from selenium
- Pre-activation -free and simple set up
- Minimal amount of solvent

3.2. Microwave-Assisted Addition to Unsaturated Bonds

Microwave irradiation provides rapid, internal heating, often resulting in higher yields and shorter reaction times compared to conventional thermal heating. Eder J. Lenardão*, Liane K. Soares, Angelita M. Barcellos and Gelson Perin* [6]. The interest in synthetic methodologies using KF/Al_2O_3 in various organic reactions focusing on the preparation of organochalcogen compounds**.** The use of this environmentally friendly reagent as an efficient and versa tile heterogeneous base to promote the addition of chalcogen nucleophiles to alkynes and, unsaturated compounds has increased in the last decade. Besides addition reactions,

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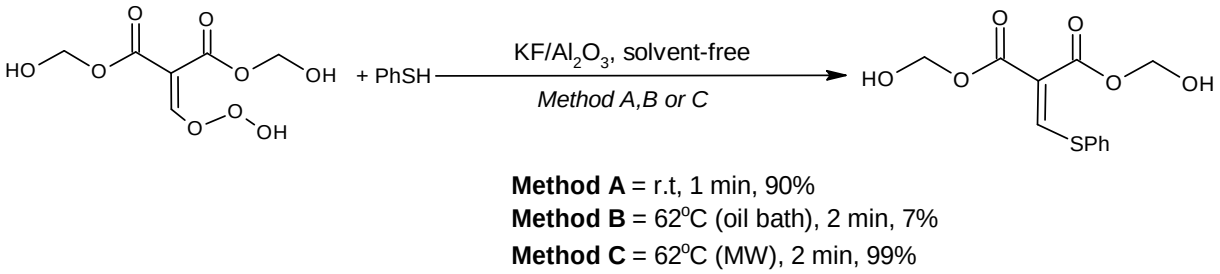
substitution, cross-coupling, condensation, cyclization, multicomponent and oxidation reactions and others are among the plethora of methods to prepare organic compounds containing selenium, tellurium or sulfur. In a general way, the reactions using KF/Al_2O_3 as the base are cleaner and faster than those using homogeneous basic catalysis. The solid supported KF is suitable to reactions under solvent-free conditions accelerated by irradiation with microwaves and can be easily recycled and reused in successive re actions, making it an excellent choice for the green synthesis of organochalcogen compounds.

Scheme 2:

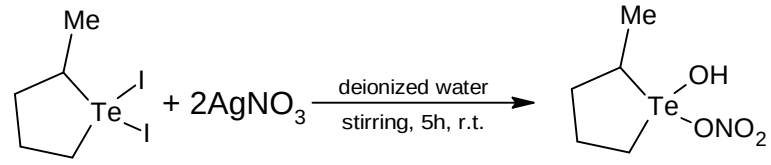


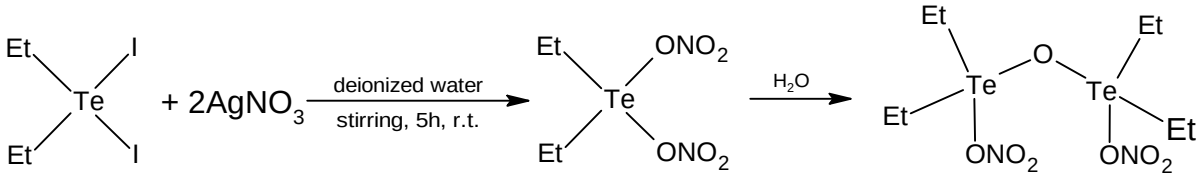
Method A = r.t, 1 min, 90%
Method B = 62°C (oil bath), 2 min, 7%
Method C = 62°C (MW), 2 min, 99%

4. Green Synthetic Methodology for OrganoTellurium (Te)

4.1. Organotellurium (IV) compounds 1-hydroxo-1-nitrato-2-methyl-1-telluracyclopentane $[C_4H_7(CH_3)\ Te(OH)(NO_3)]$ (1), m-oxo-bis[1-nitrato-1,1-diethyltellurium(IV)] $[(C_2H_5)2Te(NO_3)]_2O$ (2), spirooxalato-1- telluracyclopentane $C_4H_8Te(C_2O_4)$ (3), and 1,1-oxalato-1,1-diethyltellurium(IV) $(C_2H_5)_2Te(C_2O_4)$ (4) were synthesized. Compounds 1 and 2 were synthesized by the reactions of R_2TeI_2, [R_2 ¼ $C_4H_7(CH_3)$, $(C_2H_5)_2$] **[7]** with silver nitrate respectively in a 1:2 molar ratio in an aqueous medium at room temperature.

Scheme 3:





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4.2. Solvent-Free Synthesis

The synthesis of ditelluroxanes: l-oxo-bis[nitrato dimethyl tellurium (IV)] $[(CH_3)_2TeNO_3]_2O$ (1), l-oxo-bis[(2,4,6-trinitro)phenolato dimethyl tellurium (IV)] $[(CH_3)_2TeOC_6H_2(NO_2)_3]_2O$ (2) and l-oxo-bis[1-(2,4,6-trinitro)phenolato-1,1,2,3,4,5-hexahydrotellurophene] $[C_4H_8TeOC_6H_2(NO_2)_3]_2O$ (3) was achieved. 1 was synthesised by the reaction of $(CH_3)_2TeI_2$ with fuming HNO_3 while 2 and 3 were syn- thesised by the reactions of $R_2Te(OH)_2$ [R_2 = $(CH_3)_2$, (C_4H_8)] (*in situ*) with 2,4,6-trinitrophenol [2,4,6-$(NO_2)_3C_6H_2OH$] (picric acid).The synthesized by our group [11] .

Scheme 4*:*

$R_2TeI_2 + 2AgOH \xrightarrow{\text{Deionized water}} R_2Te(OH)_2$

Where $R_2 = (CH_3), C_4H_8$ *(In-situ)*

$R_2Te(OH)_2 \xrightarrow{\text{stirring 1 Hrs , distilled water}} [C_4H_8TeOC_6H_2(NO_2)_3]_2O$

2,4,6, Tri-Nitrophenol

5. Conclusion

The evolution of organochalcogen synthesis towards green methodology is not merely a regulatory necessity but a chemical advantage. Solvent-free and microwave-assisted techniques provide superior yields and faster reaction kinetics while drastically reducing the environmental footprint. Mechanochemistry, in particular, emerges as a frontrunner for the synthesis of symmetrical diselenides **[10]**. Future research should focus on the scale- up of these laboratory-scale green protocols to industrial levels and the exploration of bio-based catalysts (e.g., enzymes or plant extracts) for Chalcogen functionalization.

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