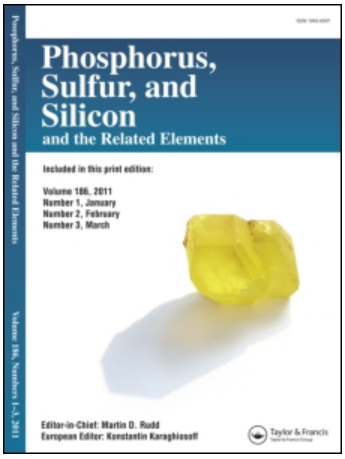

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Synthesis and Characterization of Some Bromosubstituted Symmetrical Dipyridyl Ditellurides and X-Ray Structure of 2,2'-Dipyridyl Ditelluride

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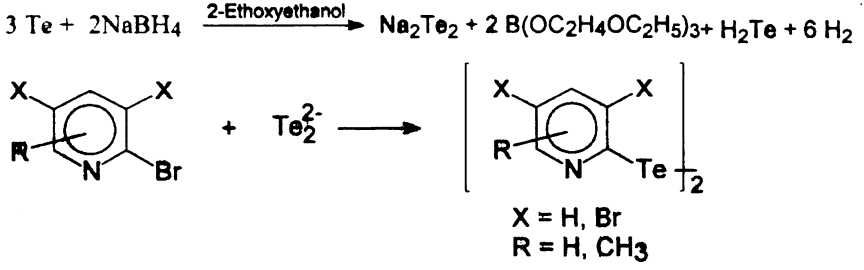
Organotellurium compounds are proving important precursors for the generation of semiconducting materials. However, synthetic methods for their preparation involve cumbersome manipulations and require controlled experimental conditions. We wish to report a convenient method recently developed for the synthesis of this interesting class of ditellurides. The title compounds were prepared by the reaction of ditelluride anion Te_2^{2-} with 2-bromopyridine (Scheme 1). The ditelluride anion was generated *in situ* by the reaction of tellurium metal with sodium borohydride in 2-ethoxyethanol. The compounds prepared were characterized by elemental analysis and through various spectroscopic techniques viz; IR, NMR (^{1}H, ^{13}C), mass spectral analysis, crystal structure of 2,2′-dipyridyl ditelluride is reported.



SCHEME 1 Preparation of bromosubstituted symmetrical dipyridyl ditellurides.

Chemical and Biochemical Aspects of Anti-Thyroid Drugs

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Thyroid gland produces thyroxine (**T4**) as the main secretory product and the monodeiodination of this prohormone to the biologically active hormone, 3,5,3′-triiodothyronine (**T3**), is the first step in thyroid hormone action. It is well known that type I iodothyronine deiodinase (ID-1), an enzyme containing selenocysteine in its active site, is responsible for most of this conversion.[1,2] The activation of thyroid stimulating hormone (TSH) receptor by auto-antibodies leads to an overproduction of thyroid hormones, which can be controlled by specific inhibitors such as 6-*n*-propyl-2-thiouracil (PTU) and methimazole (MMI) that either block the thyroid hormone biosynthesis or reduce the conversion of **T4** to **T3**.[1] Although these compounds are the most commonly employed drugs in the treatment of patients with hyperthyroidism, the detailed mechanism of their action is still not clear. It has been reported that PTU and other related compounds can block the thyroid hormone synthesis by inhibiting the iron-containing enzyme thyroid peroxidase or by reducing the conversion of **T4** to **T3**.[3–5] The mechanism of the inhibition of thyroid peroxidase by anti-thyroid drugs will be discussed.

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Convenient Synthesis of Bromo-Substituted Symmetrical and Unsymmetrical 2-Pridylselenium Compounds

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Organoselenium compounds have become increasingly important as reagents in organic synthesis and have proved to be excellent single source precursors for the generation of semi-conducting materials. A number of synthetic methods for their preparation have been developed which most frequently employ the use of expensive reducing agents and controlled experimental conditions. We wish to report a convenient synthesis of various methylsubstituted bis(5-bromo-2-pyridyl)diselenides by reacting diselenide anion Se_2^{2-}, formed by the reduction of elemental selenium with 100% hydrazine hydrate in alkaline medium, with methylsubstituted 2,5-dibromopyridines under noncryogenic conditions. The methodology successfully was extended to 2,3,5-tribromopyridine to obtain bis(3,5-dibromo-2-pyridyl) diselenide in good yield. The cleavage of selenium-selenium bond in these diselenides was achieved by using hydrazine hydrate to generate bromosubstituted pyridylselenolate anion, which reacts with haloalkane to afford 2-pyridylselenoalkane. All the compounds prepared were characterized by elemental analysis and various spectroscopic techniques viz., NMR (^{1}H, ^{13}C, ^{77}Se), and mass spectral analysis.

A Novel One-Pot Synthesis of 2-Pyridyl Chalcogenides (Se, Te) Through Bromine-Magnesium Exchange Reaction of Various 2-Bromopyridine with Tributyl Magnesium Ate Complex

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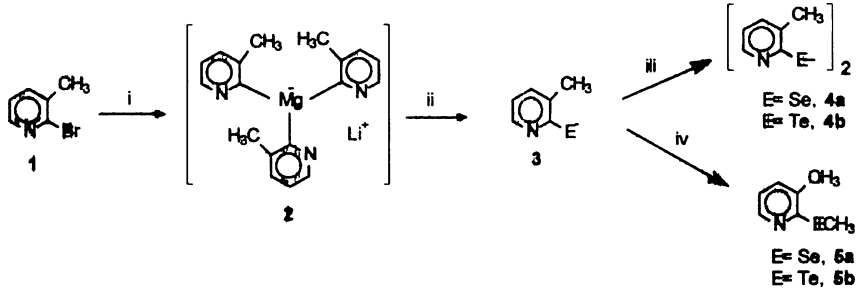
Organoselenium and -tellurium compounds, have served as starting materials for the synthesis of various organic compounds and a variety of potential anticancer, anti-inflammatory, and antioxidant drugs. These compounds have also served as single source precursors for the preparation of semi-conducting materials. While the chemistry of alky and arly selenium and tellurium compounds have been extensively studied, the scope of the corresponding pyridyl selenium and -tellurium chemistry is relatively unexplored. This is primarily due to non-availability of a convenient synthesis. The older and most frequently employed methods either involve elevated temperatures or cryogenic

conditions, which often are nonreproducible, give poor yields, and require longer time periods. Therefore the development of a practical, efficient, and quick process has been quite desirable. In this communication, we describe a novel and efficient methodology for the preparation of titled compounds, utilizing the magnesium ate complex, n-Bu_3MgCl. Scheme 1 for which is outlined below.



SCHEME 1 *Reagents and conditions*, 10.35 n-Bu_3MgCl toluene, $-10^{\circ}C$, 3h; ii E, $-10^{\circ}C$; III O_2 room temperature; iv CH_3I, $0^{\circ}C$.

Convenient Synthesis of Some Unsymmetrical Alkyl Diarylmethyl Selenides and Crystal Structure of Diphenylmethylseleno-2-Propene

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Mixed dialkyl selenides constitute an interesting class of organoselenium compounds because of their potential to act as convenient starting materials for a variety of functional group transformations. We wish to report a convenient synthesis of some unsymmetrical alkyl diarylmethyl selenides. The synthetic procedure involves the cleavage of Se—Se bond of bis(diarylmethyl)diselenide to generate the corresponding selenolate anion by sodium borohydride followed by alkylation to afford the titled compounds in moderate to high yield (Scheme 1). The

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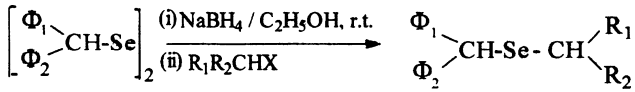

$\phi_1 = \phi_2 = C_6H_5$; $\phi_1 = p\text{-}C_6H_4Cl$, $\phi_2 = C_6H_5$
$R_1 = R_2 = H, CH_3, C_6H_5$; $X = Br, Cl$
$R_1 = H$; $R_2 = H, CH_3, CH{=}CH_2, C_6H_5, C_3H_7$

SCHEME 1

compounds thus prepared display unique chemical behavior owing to greater electronic delocalisation which renders the C—Se bond weak. This article primarily features an effective strategy to overcome the difficulties encountered in handling the lower aliphatic selenides and diselenides. The designed derivatives unlike the parent selenides and diselenides are more stable, nonfoul smelling and in some cases even stable crystalline solids. The compounds have been characterized by elemental analysis and various spectroscopic techniques viz. NMR (^{1}H, ^{13}C, ^{77}Se), FT-IR, U.V.-Vis, and mass spectrometry.

X-ray crystallographic study of diphenylmethylseleno-2-propene has been carried out.

Regioselective Synthesis of Symmetrical and Unsymmetrical Pyridyl Chalcogens (Se/Te) Using Grignard Reagents, and X-Ray Crystal Structure of Bis(2,5-Dibromo-3-pyridyl)diselenide

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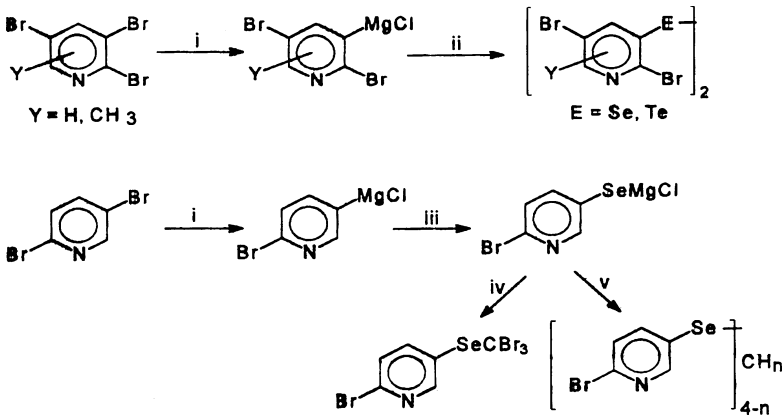
In continuation of our ongoing project on the chemistry of pyridyl chalcogens we report the regioselective synthesis of 5-pyridyl and 3-pyridyl chalcogens for the first time using Grignard reagents (Et-MgCl, i-PrMgCl and n-BuMgCl) under noncryogenic conditions. Magnesiopyridines have been generated by the selective bromine–magnesium exchange reaction of 2,5-dibromopyridine with Grignard reagents. Magnesiopyridines thus obtained react with elemental selenium or tellurium to give the corresponding pyridyl chalcogen chlorides which upon aerial oxidation give the desired dichalcogenides (Scheme 1). This



SCHEME 1 *Reagents and conditions*: I) RMgX(1.2 equiv.), THF, r.t., 2 h, ii) E, 15 mts, O_2, iii) Se, 15 mts, iv) CBr_4, and CH_nX_{4-n} (where n = 1–3).

protocol has been further extended to the preparation of hitherto unknown unsymmetrical 2-bromo-5-pyridylselenomethanes. All the compounds prepared are new and characterized by elemental analysis and various spectroscopic techniques (^{1}H, ^{13}C, ^{77}Se, ^{125}Te) NMR and mass spectral analysis. Crystal structure of some of the representative compounds were determined. The results shall be discussed.

First Examples of Heavier Chalcogenides (S and Se) of Cyclotriphosphazanes

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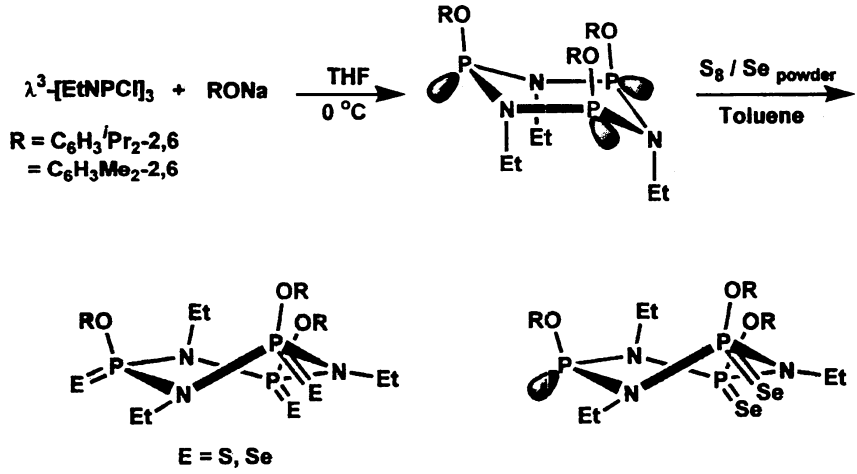
The effect of bulky substituents in kinetically stabilizing unusual compounds of heavier main group elements has been investigated over the last two decades since the selection of appropriate substituents would lead to interesting transformations in structural properties. In an attempt to assess the magnitude of substituent steric strain in determining the ring conformation and substituent disposition, we have carried out the reaction between alkali metal salts of *o,o′*-substituted phenols and λ^3-$[EtNPCl]_3$ to yield sterically croweded *cis*-λ^3-cyclotriphosphazanes $[EtNPOR]_3$ in flattened-chair conformation. The subsequent reaction of λ^3-$[EtNPOR]_3$ with excess of elemental

sulfur and selenium produces the twist-boat *cis*-λ^5-[EtNP(E)OR]$_3$ (E=S and Se) (Scheme 1). Compounds have been characterized by multinuclear NMR (^{1}H, ^{31}P, and ^{77}Se) spectroscopy and single crystal X-ray diffraction studies.



SCHEME 1

Glutathione Peroxidase-Like Antioxident Activity of Selenoenzyme Mimetics: Novel Structures and Catalytic Mechanisms

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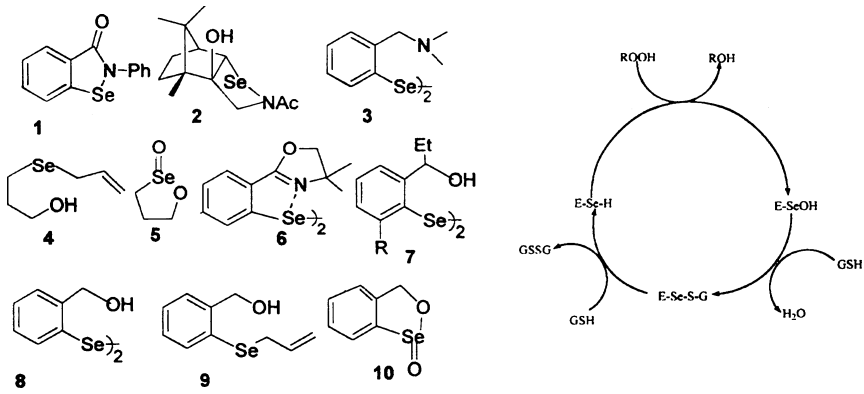
The chemical and biological importance of selenium has attracted much attention as evidenced by several model studies on the antioxidant properties of synthetic organoslenium compounds (**1–7**).[1–2] Selenenamide

2 displays strong catalytic activity in a model peroxide/thiol system (Scheme 1). Very recently Back et al.[3] have synthesized a series of alkyl diselenide and seleninate ester **5** containing Se—O bond. They observed that toxygen containing selenium compounds are also show excellent GPx-like antioxidant activity.



SCHEME 1

Herein, we report the synthesis, characterization, and GPx-like activity of the novel cyclic seleninate ester 10 generated from allyl 3-hydroxybenzyl selenide **9**, and compare its GPx-like activity with diselenides. Compounds **8** and **10** was characterized by ^{1}HNMR, multinuclear NMR spectroscopy, and X-ray crystallographic method.

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Investigations on Some Acyl(aryl)Tellurium(IV) Dihalides

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Some new acyl(aryl)tellurium(IV) dihalides. $RR'TeX_2$ (R = *p*-hydroxyphenyl, *p*-anisyl and 3-methyl-4-hydroxyphenyl: R′ = phenacyl, naphthacyl and styrylacyl and X = Br, I) have been synthesized from

respective acyl(aryl)tellurium(IV) dichlorides by halogen exchange processes. The acyl(aryl) tellurium(IV) dichlorides in turn were obtained by refluxing acetophenone, I-acetonaphthone or benzalacetone with aryltellurium trichlorides in carbon tetrachloride. Aryl tellurium trichlorides needed for the purpose were prepared by direct reactions of tellurium(IV) chloride with phenol, anisole and *o*-cresol. These acyl(aryl)tellurium(IV) dibromides and diiodides have been characterized by elemental analysis conductance, cryoscopy, infrared and far infrared spectral studies. Conductance measurements reveal their monomeric, nonelectrolyte type behavior in solutions of nitrobenzene, acetone, and acetonitrile, which is well supported by cryoscopic data in nitrobenzene. The ν_{Te-C} (acyl) and ν_{Te-C} (aryl) appear around 500 cm^{-1} and 240 cm^{-1}, respectively. The far IR spectral data suggest their monomeric nature having pseudo-trigonal bipyramidal (TBP) structure.

Convenient Synthesis, Structure of Novel Ebselen Derivatives, and their GPx-Like Catalytic Activity

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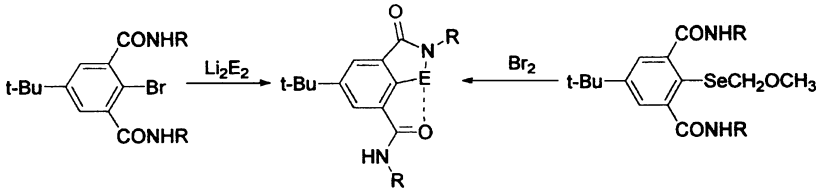
Ebselen (2-phenyl-1,2-benzisoselenazol-3(2H)-one), its derivatives and analogues are good glutathione peroxidase mimics, antiinflammatory, antiatherosclerotic, anticancer, and antimicrobial agents as well as immunostimulants, cytokine inclusers, and nitric acid synthase inhibitor.[1] Although ebselen is a major GPx mimic, its synthesis has been a challenging area.[2] A new general synthetic approach to prepare 5-t-butyl-7-alkyl/phenylcarbamoyl-2-alkyl/phenylisobenzchalcogenazol-3(2H)-one(substituted ebselen derivatives) using one-pot procedure is described here (Scheme 1). The synthesis of benzisoselenazolones is described by an additional route, i.e., treatment of corresponding methoxymethyl selenide with an equivalent of bromine. The synthesis of methoxymethyl selenides is accomplished by lithiation of bromo

precursors followed by treatment with bis(methoxymethyl) diselenide. Some of the benzisoselenazolones are characterized by single crystal X-ray technique. The GPx-like catalytic activity of compounds is determined by coupled reductase assay. Tellurium analogue showed two fold activity compared to its selenium analogue.



SCHEME 1

REFERENCES

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