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Indium(I) Iodide Promoted Cleavage of Diphenyl Diselenide and Disulfide and Subsequent Palladium(0)-Catalyzed Condensation with Vinylic Bromides. A Simple One-Pot Synthesis of Vinylic Selenides and Sulfides

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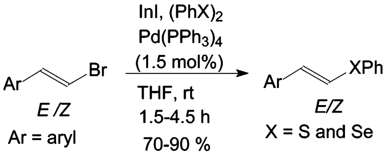
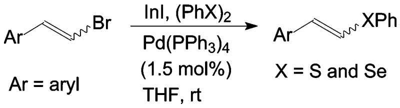


Diphenyl diselenide (and disulfide) undergo facile reaction with indium(I) iodide and the corresponding intermediate complex condenses in situ with a variety of substituted vinyl bromides in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) [Pd(PPh$_3$)$_4$] in THF at room temperature to produce vinylic selenides and sulfides in good yields. The conversion of (*E*)-vinyl bromides is remarkably stereoselective giving (*E*)-vinyl selenides (and sulpfides) whereas the stereoselectivity in reaction of (*Z*)-vinyl bromides is not very good.

During the past decade, indium metal and its trihalides have been demonstrated to be potential reagents for carbon−carbon bond formation, rearrangements, reductions, and other useful chemical transformations.[1] This led to considerable current interest to search for newer indium derivatives for novel reactions. As a part of our interest and intense involvement in this area during the past few years,[1e,2] we recently undertook an investigation to explore the application of indium(I) iodide among others and discovered the facile cleavage of diorganyl selenides and sulfides by this indium derivative and subsequent addition to alkyl halides[3a,b] and activated alkenes.[3c,d] We also observed during this study that vinylic halides remained inert in this indium(I)-mediated selenate or thiolate condensation. Further investigations now revealed that the presence of a catalytic amount of Pd(0) derivatives in the reaction mixture efficiently drives the condensation leading to the synthesis of vinyl selenides and sulfides in one pot (Scheme 1), and the results are reported here.

SCHEME 1. Synthesis of Vinyl Selenides and Sulfides



Organic selenides, in general, are of considerable interest in academia as well as in industry because of their wide involvement in organic synthesis[4a] and their useful biological activities.[4b] Among various organoselenium compounds, vinylic selenides are very useful intermediates,[5a] particularly in the synthesis of carbonyl compounds[5b] and for the stereoselective preparation of functionalized alkenes.[5] As vinyl selenides are not very easy to obtain, only a limited number of methods are available for their synthesis,[6] and in general, these are based on three general approaches, namely, hydroselenation of alkynes,[6a,b] Wittig olefination,[6c] and direct nucleophilic substitution of vinylic halides.[6d] Although these procedures are quite satisfactory, one serious limitation is in the accomplishment of one single stereoisomer of the product as all of the methods,[6] particularly hydroselenation of alkynes and Wittig olefination strategies, lead to formation of mixture of stereoisomers in varying proportions (50:50−80:20). In addition, the long reaction time (12−48 h)[6a,b] and higher temperature[6d] required for most of these methods constitute practical disadvantages. On the other hand, vinylic sulfides also have considerable synthetic utility in organic chemistry,[7] and similar protocols are used for their synthesis too.[8] Thus, considering the importance of these molecules, a milder, more stereoselective, and convenient methodology is highly desirable.

The experimental procedure for this reaction is very simple. A mixture of a substituted vinyl bromide, diphenyl diselenide

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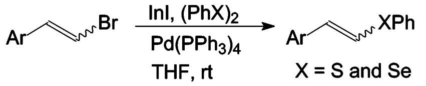
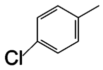
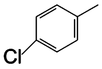
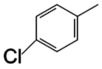
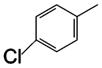
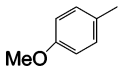
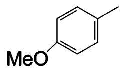
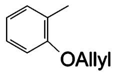
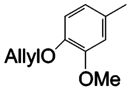
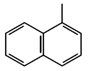
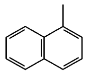
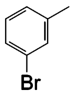
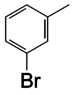
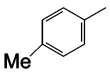
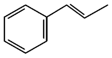
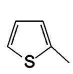
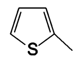
TABLE 1. Synthesis of Vinyl Selenides and Sulfides



entry	Ar	(E/Z)	X	product(s) (E : Z)	time(h)	yield(%)[a]	ref
1	Ph	(E)	Se	100:00	2.5	85	10
2	Ph	(E)	S	100:00	4.5	80	8d
3	Ph	(Z)	Se	50:50	2.5	80	10
4	Ph	(Z)	S	55:45	4.0	75	8d
5		(E)	Se	100:00	2.0	85	11
6		(E)	S	100:00	4.0	75	12
7		(Z)	Se	70:30	2.5	75	12
8		(Z)	S	54:46	4.5	70	12
9		(E)	Se	100:00	1.5	82	13
10		(E)	S	100:00	3.5	70	13
11		(E)	Se	100:00	2.0	90	
12		(E)	Se	100:00	2.5	85	
13		(E)	Se	100:00	2.0	75	
14		(E)	S	100:00	4.5	70	
15		(Z)	Se	58:42	2.5	70	
16		(Z)	S	73:27	4.5	70	
17		(Z)	Se	40:60	3.0	85	14
18		(75:25)	Se	85:15	4.0	80	6b
19		(70:30)	Se	85:15	4.0	80	
20		(70:30)	S	88:12	4.5	75	

[a] Yields refer to those of pure isolated products characterized by IR and ^{1}H and ^{13}C NMR spectroscopic data and elemental analysis.

(or disulfide), and indium(I) iodide in THF was stirred at room temperature in the presence of a catalytic amount (1.5 mol %) of Pd(PPh$_3$)$_4$ for a certain period of time (TLC). Usual workup and extraction with ether followed by a column chromatography provided the pure product.

A wide range of structurally diverse substituted vinyl bromides underwent reactions with diphenyl selenide and disulfide by this procedure to produce the corresponding vinyl selenides and sulfides in high yields. The results are presented in Table 1. Very significantly, the (*E*)-vinyl bromides furnished exclusively the (*E*)-vinyl selenides (entries 1, 5, 9, 11, 12, and 13) and sulfides (entries 2, 6, 10, and 14), whereas the (*Z*)-vinyl bromides, in general, led to a mixture of stereoisomers (*E*/*Z*) ranging from 50:50 to 70:30 (entries 3, 4, 7, 8, 15, 16, and 17). However, when the starting vinyl bromides were mixtures of stereoisomers, the products were obtained in proportionately enriched mixture also indicating the stereoselective conversion of *E* to *E* and *Z* to *Z* and *E* (entries 18 and 20). This procedure is acceptable to a variety of substituents on the aromatic ring. Interestingly, the *O*-allyl group remained intact in the presence of Pd(0) catalyst under the reaction condition (entries 11 and 12). Sensitive molecules such as thiophene derivatives also survived (entries 19 and 20).

In general, the reactions are very clean and considerably fast. The products are obtained in high purity. The ratio of stereoisomers was easily determined by analysis of coupling constants of the olefinic protons in ^{1}H NMR and relevant peaks in the ^{13}C NMR spectra. The reactions did not proceed in the absence of Pd(0), and it was observed that Pd(II) salts were not effective. Without InI and with only Pd(0) catalyst the reactions did not proceed. Interestingly, with an increased amount of catalyst the yield was reduced, and 1.5 mol % of the catalyst was found to be the most effective. We have also found that this substitution reaction was not successful using other indium reagents such as In−THF and In−TMSCl. However, in a recent report of the synthesis of chalcogenides using In intermediates in aqueous medium,[9] only one example of the formation of vinyl selenide in 60% yield by the reaction of the corresponding vinyl bromide with diphenyl diselenide by indium metal in aqueous THF and NaCl over 24 h was addressed. It may be mentioned that the present procedure using InI provides much better results in terms of yield (80%) and reaction time (2.5 h) with respect to this particular reaction (entry 1).

It is speculated that initially InI adds to diphenyl diselenide (or disulfide) to form an intermediate bis(phenylseleno/thiophenyl)iodoindium(III),[3a,b] which then interacts with the palladium complex of vinyl bromide to push the reaction toward product. The (*E*)-vinyl bromide leads to thermodynamically more stable (*E*)-isomer of the product in a straightforward way. However, in case of (*Z*)-vinyl bromide, the corresponding Se−Pd complex (III) undergoes β-elimination[8c,d] to form an alkyne−Pd intermediate (IV), which is rather free to lead to the mixture

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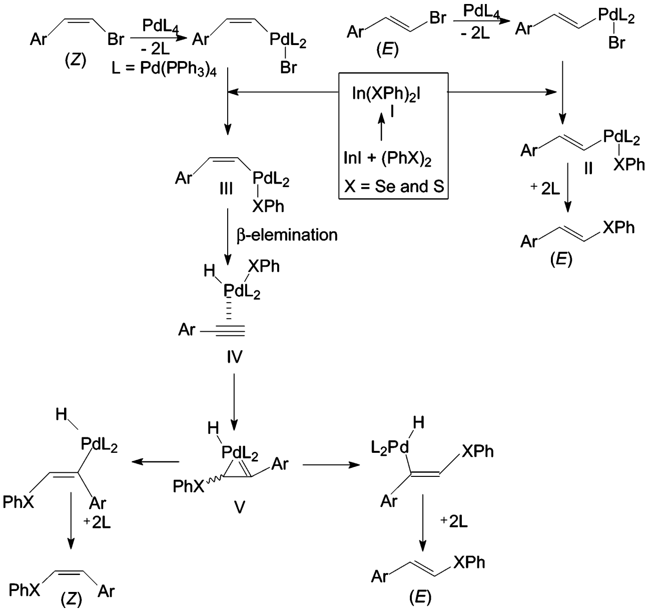
SCHEME 2. Probable Reaction Path for Formation of Vinyl Selenide/Sulfide



of either (*E*)- or (*Z*)-isomers through an η-complex V.[15] The probabale reaction path is outlined in Scheme 2.

Conclusion

In conclusion, a simple one-pot procedure for the synthesis of vinyl selenides and sulfides has been developed involving indium(I) iodide mediated cleavage of diphenyl diselenide and sulfide and subsequent reaction with vinyl bromides in the presence of Pd(0) catalyst. The notable advantages offered by this method are operational simplicity, mild reaction condition, faster reaction, exclusive stereoselectivity for (*E*)-vinyl bromides, general applicability to a wide variety of substrates, and high isolated yields of products. Thus, it provides a better and practical alternative to the existing procedures,[6,8,9] and we believe that it will find useful applications in organic synthesis. Moreover, it demonstrates the potential of indium(I) iodide in difficult organic transformations and shows great promise toward further useful applications.

Experimental Section

General Experimental Procedure for the Synthesis of Substituted Vinyl Selenides and Sulfides. Representative Procedure for (*E*)-Phenylvinyl Phenyl Selenide (Entry 1). To a stirred solution of indium(I) iodide (121 mg, 0.5 mmol) and diphenyl diselenide (156 mg, 0.5 mmol) in dry THF (2.5 mL) was added *trans*-phenylvinyl bromide (183 mg, 1 mmol) followed by $Pd(PPh_3)_4$ (18 mg, 1.5 mol %). The reaction mixture was then stirred at room temperature for 2.5 h (TLC) and quenched with a few drops of water. THF was then evaporated under vacuum, and the residue was extracted with ether (3 × 20 mL). The ether extract was washed with brine, dried (Na_2SO_4), and evaporated to leave the crude product, which was purified by column chromatography over silica gel with hexanes−ether (99:1) to furnish pure (*E*)-phenylvinyl phenyl selenide as a pale yellow oil (220 mg, 85%).

This procedure was followed for the synthesis of all products listed in Table 1. Although this procedure is described in mmol scale, a few gram scale reactions were also carried out with comparable yields. The known compounds were identified by comparison of their spectral data with those reported (Table 1), and the new compounds were properly characterized by their IR, ^{1}H NMR, and ^{13}C NMR spectroscopic data and elemental analysis.

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Supporting Information Available: Spectroscopic (IR, ^{1}H NMR, and ^{13}C NMR) data and elemental analysis of the compounds listed in entries in 11−16, 19, and 20 and ^{13}C NMR spectra of all products in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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