ORGANIC LETTERS

2003
Vol. 5, No. 9
1439−1441

Indium(I) Iodide-Mediated Cleavage of Diphenyl Diselenide. An Efficient One-Pot Procedure for the Synthesis of Unsymmetrical Diorganyl Selenides

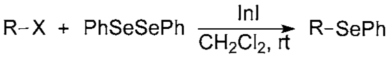
Brindaban C. Ranu,* Tanmay Mandal, and Sampak Samanta

Department of Organic Chemistry, Indian Association for the Cultivation of Science,
Jadavpur, Calcutta 700 032, India

ocbcr@iacs.res.in

Received February 1, 2003

ABSTRACT



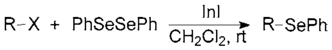
$$\text{R–X} + \text{PhSeSePh} \xrightarrow[\text{CH}_2\text{Cl}_2\text{, rt}]{\text{InI}} \text{R–SePh}$$

A simple and efficient procedure has been developed for the synthesis of unsymmetrical diorganyl selenides through a one-pot indium(I) iodide-mediated reaction of alkyl halide and diphenyl diselenide in methylene chloride at room temperature.

Indium metal and its salts have been the subject of continued interest because of their remarkable efficiency in various synthetic operations.[1] However, although the synthetic utilities of indium metal and indium(III) derivatives have been well demonstrated, indium(I) salt has been less explored.[2] As a part of our interest in indium chemistry,[1e,3] we have initiated an investigation on the use of indium(I) iodide for useful chemical transformations.

Organic selenides are of considerable interest in academia as well as in industry because of their wide involvement as key intermediates in organic synthesis and use as a food supplement.[4] On the other hand, organoselenium compounds are no longer systematically classified as toxic and, thus, much effort has been devoted toward synthesis of these compounds in recent times. Although quite a number of procedures for the synthesis of organoselenium compounds have already been published,[5] most of them, with the exception of a recent report,[5b] usually require the handling of unstable reagents, strongly basic or acidic reaction conditions, and two-step procedures. Hence, an efficient procedure involving a one-step operation under neutral conditions is in demand. We have discovered a very simple reaction of alkyl halide and diphenyl diselenide mediated by indium(I) iodide at room temperature to produce a series of unsymmetrical diorganyl selenides (Scheme 1), and the results are presented here.

Scheme 1



$$\text{R–X} + \text{PhSeSePh} \xrightarrow[\text{CH}_2\text{Cl}_2\text{, rt}]{\text{InI}} \text{R–SePh}$$

A wide range of structurally diverse alkyl halides underwent reaction with diphenyl diselenide by this procedure[6]

---

* Fax: 91-33-2473-2805.

(1) (a) Cintas, P. *Synlett* **1995**, 1087. (b) Li, C.-J. *Tetrahedron* **1996**, *52*, 5643. (c) Li, C.-J.; Chan, T. H. *Tetrahedron* **1999**, *55*, 11149. (d) Chauhan, K. K.; Frost, C. G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3015. (e) Ranu, B. C. *Eur. J. Org. Chem*. **2000**, 2343.

(2) (a) Marshall, J. A.; Grant, C. M. *J. Org. Chem*. **1999**, *64*, 696. (b) Ohno, H.; Hamaguchi, H.; Tanaka, T. *Org. Lett.* **2000**, *2*, 2161. (c) Nobrega, J. A.; Goncalves, S. M. C.; Peppe, C. *Tetrahedron Lett*. **2000**, *41*, 5779; **2001**, *42*, 4745. (d) Barros, O. S. de R.; Lang, E. S.; Oliveira, C. A. F. de.; Peppe, C.; Zeni, G. *Tetrahedron Lett*. **2002**, *43*, 7921.

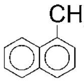
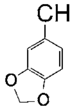
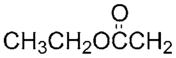
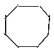
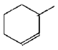
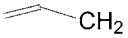
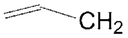
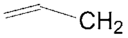
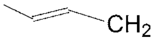
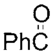
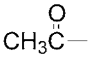
(3) (a) Ranu, B. C.; Hajra, A.; Jana, U. *J. Org. Chem*. **2000**, *65*, 6270. (b) Ranu, B. C.; Hajra, A. *J. Chem. Soc., Perkin Trans. 1* **2001**, 355. (c) Ranu, B. C.; Samanta, S.; Guchhait, S. K. *J. Org. Chem*. **2001**, *66*, 4102. (d) Ranu, B. C.; Dutta, J.; Guchhait, S. K. *J. Org. Chem*. **2001**, *66*, 5624. (e) Ranu, B. C.; Dutta, J.; Guchhait, S. K. *Org. Lett*. **2001**, *3*, 2603. (f) Ranu, B. C.; Samanta, S.; Hajra, A. *J. Org. Chem*. **2001**, *66*, 7519. (g) Ranu, B. C.; Samanta, S.; Guchhait, S. K. *J. Org. Chem*. **2001**, *66*, 4102. (h) Ranu, B. C.; Samanta, S.; Hajra, A. *Synlett* **2002**, 987. (i) Ranu B. C.; Das, A.; Samanta, S. *Synlett* **2002**, 727. (j) Ranu, B. C.; Dey, S. S.; Hajra, A. *Tetrahedron* **2002**, *58*, 2529. (k) Ranu, B. C.; Samanta, S.; Das, A. *Tetrahedron Lett*. **2002**, *43*, 5993. (l) Ranu, B. C.; Samanta, S. *Tetrahedron Lett*. **2002**, *43*, 7405. (m) Ranu, B. C.; Hajra, A.; Dey, S. S.; Jana, U. *Tetrahedron* **2003**, *59*, 813.

(4) (a) Krief, A.; Hevesi, L. In *Organoselenium Chemistry*; Springer-Verlag: Berlin, 1988; Vol. 1. (b) Krief, A. In *Comprehensive Organometallic Chemistry*; Trost, B. M., Eds.; Pergamon Press: Oxford, 1991; pp 85−192.

10.1021/ol034178c CCC: $25.00

Table 1. Synthesis of Alkyl Phenyl Selenides

$$\text{R–X} + \text{PhSeSePh} \xrightarrow[\text{CH}_2\text{Cl}_2,\ \text{rt}]{\text{InI}} \text{R–SePh}$$

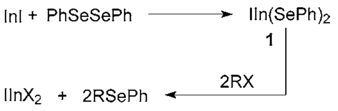
entry	R	X	time (min)	yield(%)[a]
1	$PhCH_2$	Cl	12	91
2	$PhCH_2$	Br	10	94
3	$PhCH_2$	I	5	97
4	$p(Cl)C_6H_4CH_2$	Br	10	93
5	$p(MeO)C_6H_4CH_2$	Br	30	89
6		Br	7	96
7		Br	12	87
8	PhCHMe	Br	7	93
9	$PhCH_2CH_2$	Br	60	89
10	$PhCH_2CH_2$	I	40	92
11	$CH_3(CH_2)_{10}CH_2$	Br	300	83
12	 $CH_3CH_2O\overset{O}{\overset{\|}{C}}CH_2$	Br	60	87
13		I	20	92
14		Br	10	89
15		Cl	25	87
16		Br	17	90
17		I	15	88
18		Br	30	81
19	Bu^t	Br	45	84
20	 $Ph\overset{O}{\overset{\|}{C}}–$	Cl	45	72
21	 $CH_3\overset{O}{\overset{\|}{C}}–$	Cl	40	52

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

to provide the corresponding alkyl phenyl selenides in excellent yields. The results are summarized in Table 1. Although the reactions of benzylic (entries 1−8) and allylic (entries 14−18) halides are more facile, other alkyl halides (entries 9−12) are also converted to the corresponding selenides over a longer reaction period. On the other hand, in general, bromides and iodides react faster than chlorides. Secondary (entries 8, 13) and tertiary (entry 19) bromides also undergo clean reactions. More significantly, acyl chlorides (entries 20, 21) take part in this reaction to furnish the respective phenyl selenobenzoates. However, aryl halides and vinyl halides remained inactive in this operation. The reaction conditions are sufficiently mild to be used in the presence of CO_2R, Cl, OMe, and methylenedioxy moieties.

We speculate that the reaction is going through the alkylation pathway of bis(phenylseleno)-iodo-indium(III), **1**, formed readily by reacting equimolar quantities of InI and diphenyldiselenide[2c] with alkyl halides to give the corresponding selenide (Scheme 2). The possibility of a radical pathway through indium(I)-mediated cleavage of the alkyl halide followed by addition to diphenyl diselenide is not favored, as this procedure does not allow any reaction with methyl acrylate and no dimerization product was found during formation of phenyl selenobenzoate (entry 20) by treatment of diphenyl diselenide with benzoyl chloride. The isolation of only the α-addition product from the reaction of crotyl bromide (entry 18) also supports the alkylation pathway depicted in Scheme 2.

Scheme 2



In general, the present procedure provides a relatively fast (5−60 min), clean, and high-yielding (83−97%) reaction compared to other methods.[5] A recent report[5b] using diphenyl diselenide in the presence of lanthanum metal and I_2 demonstrates virtually no reaction with tertiary alkyl halide and low yield (43% by GC) with benzoyl chloride. However, our procedure does not find any difficulty in coupling with tertiary alkyl bromide (entry 19) and reasonably good yields (isolated) are obtained with benzoyl chloride (72%) (entry 20) and acetyl chloride (52%) (entry 21).

To conclude, an efficient one-pot procedure for the synthesis of alkyl phenyl selenides has been developed through the indium(I)-mediated reaction of diphenyl diselenides with a variety of alkyl halides. This method offers significant improvements with regard to operational simplicity, reaction time, reaction conditions (room temperature and neutral medium), general applicability (coupling with tertiary alkyl halide and acyl chlorides), and high isolated yields of products, and thus it provides a better and practical alternative to the existing procedures[5] for the synthesis of diorganyl selenides. Moreover, this procedure demonstrates the syn-

---

(5) (a) Krief, A.; Derock, M. *Tetrahedron Lett*. **2002**, *43*, 3083 and references therein. (b) Nishino, T.; Okada, M.; Kuroki, T.; Watanabe, T.; Nishiyama, Y.; Sonoda, N. *J. Org. Chem*. **2002**, *67*, 8696 and references therein.

(6) **Representative Experimental Procedure (Entry 2).** To a stirred solution of benzyl bromide (171 mg, 1 mmol) and diphenyl diselenide (156 mg, 0.5 mmol) in dry methylene chloride (2 mL) was added indium(I) iodide (121 mg, 0.5 mmol) at room temperature under nitrogen. The reaction mixture was stirred for another 10 min (checked by TLC) and quenched with a few drops of H_2O. The mixture was then extracted with ether (3 × 15 mL), and the combined ether extract was washed with brine, dried (Na_2SO_4), and evaporated to leave the crude product. The crude product was purified by column chromatography over silica gel (hexane/ether 95:5) to furnish the pure benzyl phenyl selenide as a yellow liquid (232 mg, 94%), whose IR and ^1H and ^{13}C NMR spectral data are identical to those reported.[5b] This procedure was followed for the synthesis of all alkyl phenyl selenides listed in Table 1. The known compounds were identified by comparison of their spectral data with that reported,[5b] and the new compounds were properly characterized by their IR, ^1H NMR, and ^{13}C NMR spectroscopic data.

thetic potential of indium(I) iodide and provides great promise toward other useful applications.

Acknowledgment. We are pleased to acknowledge the financial support from CSIR, New Delhi [Grant 01(1739)/02] for this investigation. T.M. and S.S. are also thankful to CSIR for their fellowships.

Supporting Information Available: Spectral (IR and ^{1}H and ^{13}C NMR) data of the products (listed in entries 4−9, 12−14, 19, 21, Table 1) not reported earlier. This material is available free of charge via the Internet at http://pubs.acs.org.

OL034178C