Regioselective Markovnikov Hydrochalcogenation of Terminal Alkynes with Indium(III) Benzenechalcogenolates

Clovis Peppe,* Liérson Borges de Castro, Melina de Azevedo Mello, Olga Soares do Rego Barros

Departamento de Química, Universidade Federal de Santa Maria-UFSM, Campus UFSM, Santa Maria, RS – 97105-900, Brazil
Fax +55(55)32208031; E-mail: peppe@quimica.ufsm.br

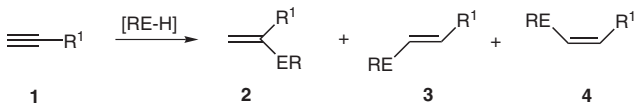
Received 18 June 2007

Abstract: Indium(III) benzenechalcogenolates (chalcogen = sulfur and selenium) promote the rigorous Markovnikov hydrochalcogenation of terminal alkynes. The generality and limitations of the reaction with aminoalkynes leading to allylic amines bearing vinylic chalcogenide substituents are discussed.

Key words: indium(III) benzenechalcogenolates, aminoalkynes, hydrochalcogenation, regioselective Markovnikov addition.

The addition of the chalcogenol constituents, REH (E = S, Se) across a triple bond of an alkyne is the simplest conceivable route to a vinyl chalcogenide. But, the rigorous regio- and stereoselective production of one of the three possible isomers from a terminal alkyne **1** (Scheme 1) is still a challenge. The direct reaction between a chalcogenol, REH (E = S, Se) and an alkyne follows a free-radical pathway and leads to a mixture of the anti-Markovnikov adducts **3** and **4**.[1] Bases with alkaline-metal counterions were shown to mediate hydrochalcogenations; the products depend on the nature of the alkyne; aromatic derivatives produce the anti-Markovnikov adducts **3** and **4** with predominancy of isomer **4** while aliphatic derivatives give rise to mixtures of isomers **2** and **4**.[2]

Only using transition-metal catalysts, rigorous regioselective protocols leading to the Markovnikov adduct **2** were disclosed.[3]

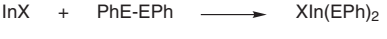


R, R^1 = alkyl or aryl; E = S, Se

Scheme 1

Recent work introduced the indium(III) chalcogenolates, obtained from the oxidative insertion of indium monohalides into the chalcogen–chalcogen bonds of diphenyl dichalcogenide (Equation 1), as useful reagents to produce new carbon–chalcogen bonds.

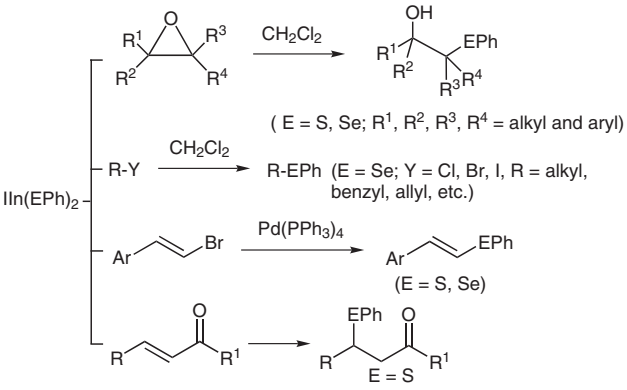
The phenylchalcogenolate species bonded to the indium(III) center is a mild nucleophile, and as such reacts in nonaqueous media with a variety of electrophiles to produce organic chemicals of interest (Scheme 2). Both,



X = Br, I; E = S, Se, Te

Equation 1

$IIn(SePh)_2$ and $IIn(SPh)_2$ promote the ring-opening reaction of epoxides to the corresponding β-hydroxy chalcogenides with rigorous regioselectivity;[4] the nucleophile incorporation at the less-hindered carbon atom was observed for alkyl-substituted epoxides, and at the benzylic carbon atom for aryl derivatives. Further, $IIn(EPh)_2$ (E = S, Se) were used to prepare unsymmetrical chalcogenides, REPh (R = alkyl and acyl) from the corresponding organyl halides.[5] Coupling with vinylic bromides was achieved under Pd(0) catalysis,[6] and Michael additions to enones were observed with the $IIn(SPh)_2$ compound.[4b]

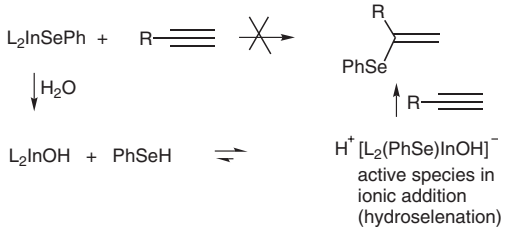


Scheme 2

The indium(III) chalcogenolates were also successfully employed to solve the problem of the Markovnikov addition leading to adducts **2**. We have demonstrated that $BrIn(SePh)_2$ promotes the hydroselenation of alkynes with remarkable stereoselectivity towards adducts **2**.[7] The reaction does not occur in anhydrous solvents, but it proceeds satisfactorily in aqueous ethanol (Scheme 3). It seems that the reaction involves an anionic complex of indium, $H[L_2(PhSe)InOH]$ formed by hydrolysis of $BrIn(SePh)_2$.

Accordingly, both compounds $IIn(EPh)_2$ (E = Se, Te) produced high yields of the Markovnikov adducts **2** from reactions with propargylic alcohols,[8] even in anhydrous solvents according to a mechanism involving as the key

SYNLETT 2008, No. 8, pp 1165–1170
Advanced online publication: 16.04.2008
DOI: 10.1055/s-2008-1072725; Art ID: S04607ST



Scheme 3

step the coordination of the alcohol, through its hydroxyl site to the indium center of the complex.

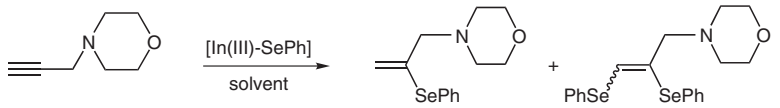
Due to the great importance of allylamines as synthetic intermediates as well as their presence in the structures of natural products and pharmaceuticals, we set out to investigate the ability of indium(III) chalcogenolates to promote hydrochalcogenation of aminoalkynes. The preparation of allylamines bearing vinylic chalcogenide substituents is very much desired, because both, vinylic sulfides or selenides undergo cross-coupling reaction with Grignard reagents catalyzed by nickel(II) salts.[9]

We were disappointed verifying that in our first attempt to hydroselenate the propargyl tertiary amine, 4-(prop-2-ynyl)morpholine (**5e**) with $IIn(SePh)_2$, no product **6′e** was obtained either in aqueous ethanol or CH_2Cl_2 solutions (Table 1, entries 1 and 2); small amount of **6′e** was obtained using the analogous indium complex $BrIn(SePh)_2$ in CH_2Cl_2 (entry 3), but no sign of **6′e** was detected in ethanol (entry 4). We have not investigated properly the reasons for this failure; we assumed that production of an ammonium halide salt derived from the propargyl amine and the indium(III) halide compound inhibited the reaction.

Indium(III) benzeneselenolate, $In(SePh)_3$ is an alternative, halide-free, and easy accessible compound containing In–Se bonds. It is readily prepared by heating the metal and diphenyl diselenide in high boiling aromatic solvents, such as toluene or xylenes.[10] We attempted to generate this compound, under Barbier conditions, from indium metal and diphenyl diselenide in aqueous ethanol (entry 5), dichloromethane (entry 6), and 1,2-dichloroethane (entry 7) solutions containing the aminoalkyne **5e**. To our satisfaction, product **6′e** was observed, although in low yields (entries 5 and 6) or contaminated with the vinylic diselenide **7′e** (entry 7). The experiments corresponding to entries 8 and 9 [in DCE–*i*-PrOH (20:1)] were conducted aiming to eliminate the production of **7′e**; both succeeded, especially the experiment conducted with previously prepared $In(SePh)_3$ (entry 9), in which product **6′e** was obtained with the satisfactory yield of 89% after 2 hours of continuous reflux.

Established the optimized reaction conditions, we set out to investigate the generality and the limitations of the hydrochalcogenation reactions of aminoalkynes **5**,[11] promoted by the $In(EPh)_3$ (E = S, Se) compounds. The results are in Table 2.[12] We first notice that there are no significant differences between the performance of the sulfur or the selenium reagents. On the other hand, the reactivity dependence on the substitution pattern in substrates **5** is striking. Terminal propargylic amines (entries 1–14) afford the Markovnikov vinylic chalcogenide. The reaction between the indium(III)-benzenethiolate with aminoalkyne **5b** was the only exception to this trend and *N*-

Table 1 Hydroselenation of **5e** under Various Reaction Conditions



5e **6'e** **7'e**

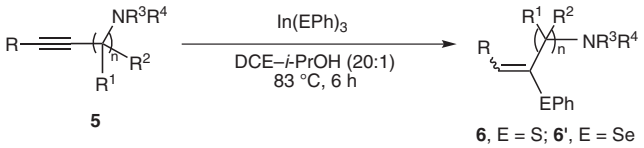
	[In(III)SePh]	Solvent	Conditions	Yields of **6′e**:**7′e** (%)[a]
1	$IIn(SePh)_2$	CH_2Cl_2	40 °C, 24 h	0:0
2	$IIn(SePh)_2$	EtOH (95%)	78 °C, 24 h	0:0
3	$BrIn(SePh)_2$	CH_2Cl_2	40 °C, 24 h	10:0
4	$BrIn(SePh)_2$	EtOH (95%)	78 °C, 12 h	0:0
5	$In(SePh)_3$[b]	EtOH(95%)	78 °C, 18 h	25:0
6	$In(SePh)_3$[b]	CH_2Cl_2	40 °C, 12 h	55:0
7	$In(SePh)_3$[b]	DCE	83 °C, 12 h	75:7
8	$In(SePh)_3$[b]	DCE–*i*-PrOH (20:1)	83 °C, 6 h	87:0[c]
9	$In(SePh)_3$[d]	DCE–*i*-PrOH (20:1)	83 °C, 2 h	89:0[c]

[a] Estimated by ^1H NMR spectroscopy.
[b] Under Barbier conditions, with $In(SePh)_3$ prepared in situ from indium metal and $(PhSe)_2$.
[c] Isolated yield of analytically pure product.
[d] $In(SePh)_3$ previously prepared.

[2,2-bis(phenylthio)propyl]-4-methylbenzenesulfonamide was obtained as a secondary product. No sign of products were obtained from aminoalkynes **5** containing internal triple bonds (entries 21 and 22). Nonpropargylic aminoalkynes (entries 17–20) either did not react with the indium chalcogenolates (entries 17 and 18) or produced smaller yields compared to the propargylic derivatives (entries 19 and 20).[13] The degree of substitution at the propargylic carbon atom in substrates **5** (R^1, R^2) dramatically affects reactivity; the higher the degree of substitution at this site, the smaller were the yields obtained (entries 1–12 vs. 13 and 14); and it is important to notice the complete inhibition of reaction with the aminoalkyne **5h** containing a quaternary propargylic carbon atom.

After examining the scope of the protocol leading to the Markovnikov adducts **6**, we searched for the origin of the diselenated byproduct **7′e**, detected during the optimization experiments (Table 1). We assumed that compound **7′e** was derived from an indium acetylide, which have been proposed in the reaction of indium(III) salts with alkynes in the presence of amines as proton acceptors.[15] The experiments described in Scheme 4 support this proposition, the indium acetylide was captured by two differ-

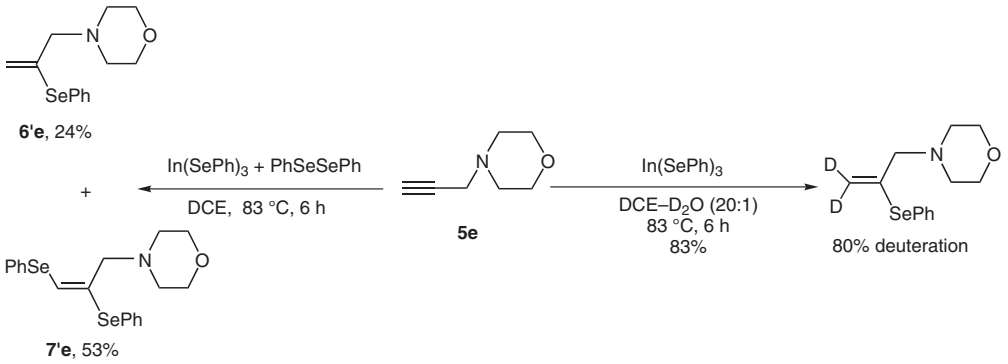
Table 2 Investigations of the Generality and Limitations of the Hydrochalcogenation Reactions of Aminoalkynes **5** Promoted by the $In(EPh)_3$ (E = S, Se) Compounds



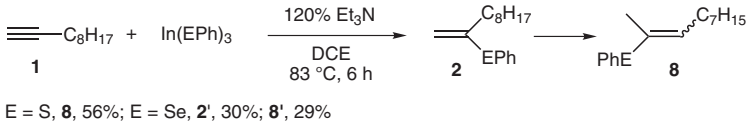
5 **6**, E = S; **6′**, E = Se

Entry	Product	R	R^1	R^2	R^3	R^4	n	Yield (%)[a]
1	**6a**[b]	H	H	H	H	H	1	62
2	**6′a**[b]	H	H	H	H	H	1	65
3	**6b**	H	H	H	Ts	H	1	67[c]
4	**6′b**	H	H	H	Ts	H	1	75
5	**6c**[b]	H	H	H	Me	H	1	62
6	**6′c**[b]	H	H	H	Me	H	1	46
7	**6d**	H	H	H	Et	Et	1	72
8	**6′d**	H	H	H	Et	Et	1	57
9	**6e**	H	H	H	$-(CH_2)_2O(CH_2)_2-$		1	90
10	**6′e**	H	H	H	$-(CH_2)_2O(CH_2)_2-$		1	89
11	**6f**	H	H	H	$-(CH_2)_5-$		1	76
12	**6′f**	H	H	H	$-(CH_2)_5-$		1	74
13	**6g**	H	H	n-C_5H_{11}	$-(CH_2)_2O(CH_2)_2-$		1	20
14	**6′g**	H	H	n-C_5H_{11}	$-(CH_2)_2O(CH_2)_2-$		1	17
15	**6h**	H	Me	Me	$-(CH_2)_4-$		1	0
16	**6′h**	H	Me	Me	$-(CH_2)_4-$		1	0
17	**6i**	H	H	H	$-(CH_2)_2O(CH_2)_2-$		2	0
18	**6′i**	H	H	H	$-(CH_2)_2O(CH_2)_2-$		2	0
19	**6j**[d]	H	H	H	$-(CH_2)_2O(CH_2)_2-$		3	36
20	**6′j**[d]	H	H	H	$-(CH_2)_2O(CH_2)_2-$		3	38
21	**6k**	n-Bu	H	H	Et	Et	1	0
22	**6′k**	n-Bu	H	H	Et	Et	1	0

[a] Isolated yield of analytically pure product.
[b] Reaction at 45 °C.
[c] Plus 27% of *N*-[2,2-bis(phenylthio)propyl]-4-methylbenzenesulfonamide.
[d] Yield after 24 h.



Scheme 4

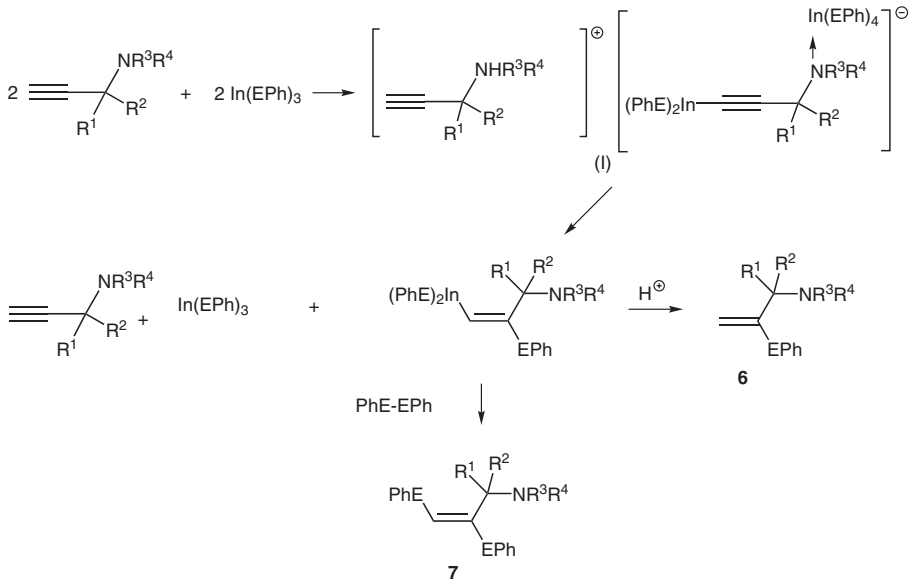


Scheme 5

ent electrophiles; deuterated water gave 83% of the dideuterated vinylselenide **6′e** (80% of deuteration),[16] and diphenyldiselenide reacted with the indium acetylide, in anhydrous 1,2-dichloroethane, to produce the *E*-diselenated byproduct **7′e** in 53% of yield together with the vinylic selenide **6′e**.[17]

To gain a deeper insight into the reactivity of the indium(III) chalcogenolates, we have examined their reactions with *n*-decyne and phenylacetylene in dichloroethane under a dry nitrogen atmosphere. Both, the sulfur and selenium compounds fail to react, even after prolonged heating. However, upon addition of triethylamine (1.2 mol equiv), the hydrochalcogenation of *n*-decyne was observed (Scheme 5), producing initially and accordingly to our previous studies,[7] the Markovnikov adducts **2** that undergo isomerization to the internal vinylic chalcogenides **8**, isolated as a mixture of isomers.[18] The failure of phenylacetylene to react under an oxygen-free atmosphere was also observed before, when we determined a diselenation reaction of its triple bond promoted by benzeneseleno radical obtained by exposing benzeneselenol to molecular oxygen.[7]

Although the mechanism of this reaction is still uncertain, there are a number of experimental facts supporting a preliminary picture. The pathway seems to involve an indium acetylide intermediate, captured by two different electrophiles (D_2O and PhSeSePh) and suggested by the need of triethyl amine acting as a base to promote the reaction with *n*-decyne. We also notice that indium-mixed complexes containing halide and chalcogenolate ligands [$XIn(EPh)_2$; X = Br, I, E = S, Se] are ineffective, probably due to precipitation of an ammonium cation during generation of the indium acetylide. Finally, we propose a coordination of the aminoalkyne through its nitrogen basic



Scheme 6

center to the indium(III) chalcogenolate responsible for transferring the chalcogenolate nucleophile, as strongly suggested by the low yields obtained with aminoalkynes containing tertiary propargylic carbon atoms and by the ineffective reaction with the quaternary aminoalkyne **5h**.

Scheme 6 illustrates how we envisage this reaction, giving a preliminary pathway which is in agreement with the experimental details discussed above, although the structure of the key intermediate, anion (I), was not established.

For this to end, we note that we have introduced new species of indium(III) chalcogenolates, $In(EPh)_3$ (E = S, Se), capable of the Markovnikov hydrochalcogenation of terminal alkynes. The addition is fairly broad in scope and generally works well especially with terminal propargyl amines. The products, allylic amines bearing vinylic chalcogenide substituents, seem to be valuable synthetic intermediates for further elaborations.

Acknowledgment

C.P. is grateful to CNPq for financial support. CAPES (to L.B.D.) and CNPq (to M.D.M. and O.S.D.B.) are acknowledged for the award of scholarships.

References and Notes

(1) For radical addition of thiols into alkynes, see: (a) Mitsudo, T.; Kondo, T. *Chem. Rev.* **2000**, *100*, 3205 and references therein. For selenols: (b) Comasseto, J. V.; Ferreira, J. T. B. *J. Organomet. Chem.* **1981**, *216*, 287.

(2) For cesium thiolates, see: (a) Kondoh, A.; Takami, K.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2005**, *70*, 6468. For sodium thiolates, see: (b) Truce, W. E.; Tichenor, G. J. W. *J. Org. Chem.* **1972**, *37*, 2391. (c) Truce, W. E.; Simms, J. A.; Boudakian, M. M. *J. Am. Chem. Soc.* **1956**, *78*, 695. (d) Truce, W. E.; Simms, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 2756. For lithium selenolates, see: (e) Zeni, G.; Stracke, M. P.; Nogueira, C. W.; Braga, A. L.; Menezes, P. H.; Stefani, H. A. *Org. Lett.* **2004**, *6*, 1135.

(3) For hydroselenation catalyzed by Pd and Pt compounds, see: (a) Ananikov, V. P.; Malyshev, D. A.; Beletskaya, I. P.; Aleksandrov, G. G.; Eremenko, I. L. *J. Organomet. Chem.* **2003**, *679*, 162. (b) Kamiya, I.; Nishinaka, E.; Ogawa, A. *J. Org. Chem.* **2005**, *70*, 696. For hydrothiolation catalyzed by nickel(II) compounds, see: (c) Ananikov, V. P.; Malyshev, D. A.; Beletskaya, I. P.; Aleksandrov, G. G.; Eremenko, I. L. *Adv. Synth. Catal.* **2005**, *347*, 1993. (d) Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P. *Organometallics* **2006**, *25*, 1970. For hydrothiolation catalyzed by Pd compounds, see: (e) Ogawa, A.; Ikeda, A.; Kimura, K.; Hirao, T. *J. Am. Chem. Soc.* **1999**, *121*, 5108; and references therein. (f) Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P.; Khrustalev, V. N.; Antipin, M. Y.; Timofeeva, T. V. *J. Am. Chem. Soc.* **2007**, *129*, 7252. For hydrothiolation catalyzed by a rhodium compound, see: (g) Cao, C.; Fraser, L. R.; Love, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 17614.

(4) For β-hydroxyselenides, see: (a) Barros, O. S. D.; de Carvalho, A. B.; Lang, E. S.; Peppe, C. *Lett. Org. Chem.* **2004**, *1*, 43. For β-hydroxysulfides, see: (b) Ranu, B. C.; Mandal, T. *Can. J. Chem.* **2006**, *84*, 762.

(5) Ranu, B. C.; Mandal, T. *J. Org. Chem.* **2004**, *69*, 5793.

(6) Ranu, B. C.; Chattopadhyay, K.; Banerjee, S. *J. Org. Chem.* **2006**, *71*, 423.

(7) Peppe, C.; Lang, E. S.; Ledesma, G. N.; de Castro, L. B.; Barros, O. S. D.; Mello, P. D. *Synlett* **2005**, 3091.

(8) For hydroselenation, see: (a) Barros, O. S. D.; Lang, E. S.; de Oliveira, C. A. F.; Peppe, C.; Zeni, G. *Tetrahedron Lett.* **2002**, *43*, 7921. For hydrotelluration, see: (b) Barros, O. S. D.; Lang, E. S.; Peppe, C.; Zeni, G. *Synlett* **2003**, 1725.

(9) (a) Gerard, J.; Hevesi, L. *Tetrahedron* **2001**, *57*, 9109. (b) Okamura, H.; Miura, M.; Takei, H. *Tetrahedron Lett.* **1979**, *20*, 43. (c) Okamura, H.; Miura, M.; Kosugi, K.; Takei, H. *Tetrahedron Lett.* **1980**, *21*, 87.

(10) Annan, T. A.; Kumar, R.; Mabrouk, H. E.; Tuck, D. G.; Chadha, R. K. *Polyhedron* **1989**, *8*, 865.

(11) (a) Aminoalkynes **5a**,**d**–**f** were prepared from propargyl bromide and the corresponding amine, **5h** was prepared from 3-chloro-3-metyl-1-butyne according to: Hennion, G. F.; Nelson, K. W. *J. Am. Chem. Soc.* **1957**, *79*, 2142. (b) Compounds **5g**,**i**,**j** were prepared from the corresponding propargyl *p*-toluenosulfonate and dialkylamines according to: Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: New York, **1988**. (c) Compound **5b** was prepared from propargylamine **5a** according to: Lo, M. M.-C.; Neumann, C. S.; Nagayama, S.; Perlstein, E. O.; Schreiber, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 16077. (d) Compound **5c** was obtained commercially from Aldrich.

(12) **General Procedure for the Markovnikov Hydrochalcogenation of the Aminoalkynes**
A Schlenk tube equipped with a reflux condenser, under N_2 atmosphere, was charged with DCE (2 mL), *i*-PrOH (0.1 mL), aminoalkyne **5** (1 mmol), and $In(EPh)_3$ (1 mmol). The mixture was heated, under reflux, for 6 h. At the end of this period, the reaction was quenched with H_2O (10 mL), the organics extracted with CH_2Cl_2 (2 × 15 mL). The extract was dried (Na_2SO_4) and evaporated to dryness under vacuum. The oily residue was purified by column chromatography (SiO_2, hexanes–EtOAc) to produce the adducts **6** and **6′** as heavy oils and in yields given in Table 2.
Spectroscopic Data for Compounds 6
2-(Phenylthio)prop-2-en-1-amine (**6a**):[19] ^{1}H NMR ($CDCl_3$): δ = 7.54–7.17 (m, 5 H), 5.31 (t, *J* = 1.2 Hz, 1 H), 4.98 (s, 1 H), 3.28 (s, 2 H), 1.82 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ = 136.96, 132.51, 129.08, 128.60, 127.65, 113.59, 46.87.
2-(Phenylseleno)prop-2-en-1-amine (**6′a**): ^{1}H NMR ($CDCl_3$): δ = 7.43 (m, 2 H), 7.18 (m, 3 H), 5.61 (s, 1 H), 5.19 (s, 1 H), 3.30 (s, 2 H), 1.70 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ = 144.50, 133.89, 128.98, 128.15, 127.47, 116.45, 48.37.
4-Methyl-*N*-(2-(phenylthio)allyl)benzenesulfonamide (**6b**): ^{1}H NMR ($CDCl_3$): δ = 7.62 (m, 2 H), 7.19 (m, 7 H), 5.35 (s, 1 H), 5.03 (s, 1 H), 3.56 (s, 2 H), 2.31 (s, 3 H). Fast decomposition in $CDCl_3$ solution prevented the recording of a satisfactory ^{13}C NMR spectrum.
N-[2,2-Bis(phenylthio)propyl]-4-methylbenzenesulfonamide (secondary product): ^{1}H NMR ($CDCl_3$): δ = 7.71 (m, 2 H), 7.45 (m, 4 H), 7.37 (m, 2 H), 7.30 (m, 6 H), 5.13 (t, *J* = 6.0 Hz, 1 H), 2.98 (d, *J* = 6.0 Hz, 2 H), 2.36 (s, 3 H), 1.19 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ = 143.45, 136.91, 136.50, 129.85, 129.68, 129.60, 128.80, 127.04, 61.41, 50.58, 25.64, 21.47.
4-Methyl-*N*-[2-(phenylseleno)allyl]benzenesulfonamide (**6′b**): ^{1}H NMR ($CDCl_3$): δ = 7.61 (m, 2 H), 7.32 (m, 2 H), 7.18 (m, 5 H), 5.67 (s, 1 H), 5.25 (s, 1 H), 3.60 (s, 2 H), 2.32 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ = 143.32, 136.78, 136.71, 133.85, 129.50, 129.27, 127.86, 127.62, 127.02, 120.61, 48.69, 21.39.
N-Methyl-2 (phenylthio)prop-2-en-1-amine (**6c**): ^{1}H NMR ($CDCl_3$): δ = 7.38–7.18 (m, 5 H), 5.26 (s, 1 H), 4.96 (s, 1 H),

3.23 (s, 2 H), 2.29 (s, 3 H), 1.64 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ = 143.72, 132.88, 132.60, 129.06, 127.73, 114.68, 55.84, 34.92.

N-Methyl-2 (phenylseleno)prop-2-en-1-amine (**6′c**) ^{1}H NMR ($CDCl_3$): δ = 7.47 (m, 2 H), 7.22 (m, 3 H), 5.60 (s, 1 H), 5.14 (s, 1 H), 3.29 (s, 2 H), 2.29 (s, 3 H), 1.83 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ = 141.59, 134.62, 129.20, 128.35, 127.81, 117.71, 57.40, 34.92.

N,*N*-Diethyl-2 (phenylthio)prop-2-en-1-amine (**6d**):[20] ^{1}H NMR ($CDCl_3$): δ = 7.43–7.20 (m, 5 H), 5.26 (s, 1 H), 4.73 (s, 1 H), 3.14 (s, 2 H), 2.50 (q, *J* = 7.1 Hz, 4 H), 0.95 (t, *J* = 7.1 Hz, 6 H). ^{13}C NMR ($CDCl_3$): δ = 145.24, 133.81, 133.05, 129.03, 127.86, 112.44, 58.33, 46.61, 11.54.

N,*N*-Diethyl-2 (phenylseleno)prop-2-en-1-amine (**6′d**): ^{1}H NMR ($CDCl_3$): δ = 7.53 (m, 2 H), 7.23 (m, 3 H), 5.55 (s, 1 H), 4.79 (s, 1 H), 3.24 (s, 2 H), 2.50 (q, *J* = 7.1 Hz, 4 H), 0,97 (t, *J* = 7.1 Hz, 6 H). ^{13}C NMR ($CDCl_3$): δ = 144.57, 135.85, 131.49, 129.11, 127.89, 113.83, 59.91, 46.45, 11.60.

4-[2-(Phenylthio)allyl]morpholine (**6e**): ^{1}H NMR ($CDCl_3$): δ = 7.39 (m, 2 H), 7.25 (m, 3 H), 5.20 (s, 1 H), 4.72 (s, 1 H), 3.65 (m, 4 H), 3.04 (s, 2 H), 2.37 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ = 143.36, 134.15, 132.48, 129.06, 128.13, 112.84, 66.89, 63.86, 53.14.

4-[2-(Phenylseleno)allyl]morpholine (**6′e**): ^{1}H NMR ($CDCl_3$): δ = 7.52 (m, 2 H), 7.23 (m, 3 H), 5.51 (s, 1 H), 4.80 (s, 1 H), 3.64 (m, 4 H), 3.14 (s, 2 H), 2.38 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ = 142.42, 136.03, 129.11, 128.40, 128.07, 114.44, 66.93, 65.30, 53.13.

1-[2-(Phenylthio)allyl)]piperidine (**6f**): ^{1}H NMR ($CDCl_3$): δ = 7.39 (m, 2 H), 7.24 (m, 3 H), 5.23 (s, 1 H), 4.74 (s, 1 H), 3.02 (s, 2 H), 2.33 (m, 4 H), 1.53 (m, 4 H), 1.36 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ = 143.77, 133.96, 132.88, 129.06, 127.99, 112.90, 64.10, 54.18, 25.77, 24.25.

1-[2-(Phenylseleno)allyl)]piperidine (**6′f**): ^{1}H NMR ($CDCl_3$): δ = 7.53 (m, 2 H), 7.23 (m, 3 H), 5.51 (s, 1 H), 4.80 (s, 1 H), 3.11 (s, 2 H), 2.34 (m, 4 H), 1.53 (m, 4 H), 1.37 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ = 143.23, 135.96, 129.11, 128.87, 127.96, 114.10, 65.54, 54.20, 25.83, 24.27.

4-[2-(Phenylthio)oct-1-en-3-yl]morpholine (**6g**): ^{1}H NMR ($CDCl_3$): δ = 7.40 (m, 2 H), 7.25 (m, 3 H), 5.00 (s, 1 H), 4.46 (s, 1 H), 3.65 (t, *J* = 4.6 Hz, 4 H), 2.80 (dd, *J* = 7.8, 6.1 Hz, 1 H), 2.49 (m, 4 H), 1.62 (m, 2 H), 1.24 (m, 6 H), 0.82 (t, *J* = 6.5 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 147.61, 136.62, 129.18, 128.58, 128.14, 113.58, 72.22, 67.18, 50.85, 31.85, 29.67, 26.32, 22.52, 14.01.

4-[2-(Phenylseleno)oct-1-en-3-yl]morpholine (**6′g**): ^{1}H NMR ($CDCl_3$): δ = 7.51 (m, 2 H), 7.25 (m, 3 H), 5.41 (s, 1 H), 4.68 (s, 1 H), 3.65 (t, *J* = 4.5 Hz, 4 H), 2.79 (dd, *J* = 8.2, 5.6 Hz, 1 H), 2.50 (m, 4 H), 1.56 (m, 2 H), 1.23 (m, 6 H), 0.82 (t, *J* = 6.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 147.62, 135.18, 132.07, 129.17, 128.41, 110.38, 71.49, 67.15, 50.85, 31.79, 29.87, 26.03, 22.50, 13.99.

4-[4-(Phenylthio)pent-4-enyl]morpholine (**6j**): ^{1}H NMR ($CDCl_3$): δ = 7.37–7.20 (m, 5 H), 5.09 (s, 1 H), 4.83 (s, 1 H), 3.63 (m, 4 H), 2.36 (m, 4 H), 2.23 (m, 4 H), 1.67 (quint, *J* = 7.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 145.26, 133.07, 129.09, 128.54, 127.77, 113.29, 66.71, 57.86, 53.49, 34.10, 24.92.

4-[4-(Phenylseleno)pent-4-enyl]morpholine (**6′j**): ^{1}H NMR ($CDCl_3$): δ = 7.45 (m, 2 H), 7.23 (m, 3 H), 5.43 (s, 1 H), 5.08 (s, 1 H), 3.64 (m, 4 H), 2.37 (m, 4 H), 2.28 (t, *J* = 7.5 Hz, 2 H), 2.23 (t, *J* = 7.5 Hz, 2 H), 1,67 (quint, *J* = 7.5 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 142.29, 134.54, 129.20, 128.65, 127.79, 117.19, 66.36, 57.64, 53.27, 35.76, 24.83.

(13) We have searched for the reasons leading to this failure. From the reaction involving homopropargylamine **5i** and $In(SePh)_3$, we have isolated after 24 h of continuous reflux 1,2-bis(phenylseleno)ethane ($PhSeCH_2CH_2SePh$) in 62% of yield based on **5i**. ^{1}H NMR ($CDCl_3$): δ = 7.35 (m, 4 H), 7.17 (m, 6 H), 3.05 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ = 133.04, 131.45, 129.14, 127.21, 27.16.[14] Bis(phenylseleno)ethane was similarly prepared by heating $In(SePh)_3$, Et_3N in DCE in 40% of yield. These facts strongly suggest parallel reactions between aminoalkynes **5i** and **5j** with DCE to form quaternary ammonium derivatives that inhibit or reduce the efficiency of the hydrochalcogenation reactions.

(14) Gulliver, D. J.; Hope, E. G.; Levason, W. *J. Chem. Soc., Perkin Trans. 2* **1984**, 429.

(15) (a) Sakai, N.; Kanada, R.; Hirasawa, M.; Konakahara, T. *Tetrahedron* **2005**, *61*, 9298. (b) Sakai, N.; Hirasawa, M.; Konakahara, T. *Tetrahedron Lett.* **2003**, *44*, 4171.

(16) 4-[3,3-Dideuterio-2-(phenylseleno)allyl]morpholine was prepared, in 83% of yield, according to the general method described above using D_2O as the deuterium source: ^{1}H NMR ($CDCl_3$): δ = 7.52 (m, 2 H), 7.23 (m, 3 H), 5.51 (s, 0.2 H), 4.80 (s, 0.2 H), 3.64 (m, 4 H), 3.14 (s, 2 H), 2.38 (m, 4 H).

(17) (*E*)-4[2,3-Bis(phenylseleno)allyl]morpholine (**7′e**) was prepared in 53% of yield together with **6′e** (24%) from aminoalkyne **5e** (1 mmol), $In(SePh)_3$ (1 mmol), and diphenyl diselenide (2 mmol) in anhyd DCE (4 mL) using the general procedure described in ref. 12.

Spectroscopic Data for 7′e

^{1}H NMR ($CDCl_3$): δ = 7.48 (m, 2 H), 7.33 (m, 2 H), 7.22 (m, 3 H), 7.18 (m, 3 H), 6.67 (s, 1 H), 3.67 (m, 4 H), 3.22 (s, 2 H), 2.42 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ = 134.33, 133.04, 131.55, 129.53, 129.28, 129.21, 129.08, 127.84, 126.95, 123.81, 66.80, 63.26, 52.97; 2D-NOE: no effect involving the singlet at δ = 6.67 ppm as required by the *E*-stereoisomer.

(18) **Spectroscopic Data for the Products of Hydrochalcogenation of *n*-Decyne with Indium(III) Benzenechalcogenolates**

2-Phenylselenodec-1-ene (**2′**):[7] ^{1}H NMR ($CDCl_3$): δ = 7.48 (m, 2 H), 7.22 (m, 3 H), 5.43 (s, 1 H), 5.04 (s, 1 H), 2.21 (t, *J* = 7.3 Hz, 2 H), 1.47 (quint, *J* = 7.3 Hz, 2 H), 1.20 (br s, 10 H), 0.82 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR ($CDCl_3$): δ = 143.5, 134.67, 129.13, 129.04, 127.65, 116.07, 38.32, 31.83, 29.32, 29.19, 28.81, 28.67, 22.64, 14.09.

(*Z*)- + (*E*)-2-Phenylselenodec-2-ene (**8′**; isolated as an unassigned 3:2 mixture of isomers): ^{1}H NMR ($CDCl_3$): δ = 7.38 (m, 2 H), 7.16 (m, 3 H), 5.89 (t, *J* = 7.3 Hz, 0.4 H), 5.71 (t, *J* = 7.1 Hz, 0.6 H), 2.18 (q, *J* = 7.1 Hz, 1.2 H), 2.03 (q, *J* = 7.3 Hz, 0.8 H), 1.92 (s, 3 H), 1.32 (quint, *J* = 7.3 Hz, 2 H), 1.21 (m, 8 H), 0.81 (t, *J* = 7.3 Hz, 1.2 H), 0.80 (t, *J* = 7.3 Hz, 1.8 H).

(*Z*)- + (*E*)-2-Phenylthiodec-2-ene (**8**, isolated as an unassigned 1:1 mixture of isomers): ^{1}H NMR ($CDCl_3$): δ = 7.34 (m, 5 H), 5.95 (tq, *J* = 7.3 Hz, 1.2 Hz, 0.5 H), 5.89 (tq, *J* = 7.3 Hz, 1.2 Hz, 0.5 H), 2.38 (q, *J* = 7.2 Hz, 1 H), 2.19 (q, *J* = 7.3 Hz, 1 H), 1.97 (d, *J* = 1.2 Hz, 1.5 H), 1.94 (d, *J* = 1.2 Hz, 1.5 H), 1.47 (m, 2 H), 1.35 (m, 8 H), 0.95 (m, 3 H).

(19) Kuniyasu, H.; Ogawa, A.; Sato, K.-I.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902.

(20) Kawakita, M.; Yokota, K.; Akamatsu, H.; Irisawa, S.; Morikawa, O.; Konishi, H.; Kobayashi, K. *J. Org. Chem.* **1997**, *62*, 8015.