

Convenient synthesis of alkynyl aryl seleno- and telluro-ethers

Darren J. Cook, Anthony F. Hill*[†] and D. James Wilson

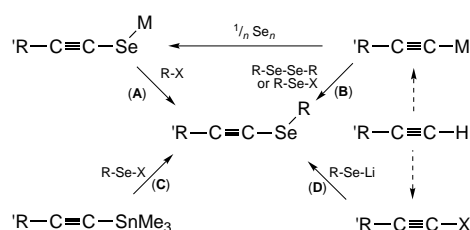
Centre for Chemical Synthesis, Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY

The reaction of bis(alkynyl)mercurials [Hg(C≡CR)₂] (R = C₆H₅, C₆H₄Me-4 or ferrocenyl) with diaryl dichalcogenides (ER')₂ (E = Se, R' = C₆H₅ or C₆H₄Cl-4; E = Te, R' = C₆H₅) conveniently provided high yields of the alkynyl aryl chalcogenoethers RC≡CER'.

Miller and Angelici¹ elegantly demonstrated the migratory aptitude and synthetic versatility of alkynyl thiolate substituents when bound to divalent ruthenium. It may be anticipated that alkynyl selenoethers will display a similarly rich organo-transition-metal chemistry, although to date very few reports of such ligands have appeared, *e.g.* the mononuclear complex [Mo(η-PhC≡CSeBu)Cl₄(SEt₂)₂]² and the dicobaltatetrahydrides [Co₂(μ-RSeCCR')(CO)₆]³. We have very recently succeeded in constructing alkynyl selenoether ligands within the coordination spheres of tungsten and molybdenum complexes *via* the facile alkylation of selenoketenyl ligands.⁴ Further investigations into the co-ordination chemistry of alkynyl selenoethers would be facilitated by convenient synthetic procedures for their preparation. Within the broader context of organic synthesis, alkynyl derivatives of selenium have attracted attention for a number of reasons, including their use as precursors to vinyl selenides⁵ and due to the potential nucleofugacity of the selenolate group (synthon for RC≡C⁺).⁶ Whilst various routes exist for these alkynes (Scheme 1),^{3,7-10} all involve the use of air- or moisture-sensitive intermediates and some present difficulties in the removal of side products. Route (A), perhaps the most convenient, involves the reaction of alkynyl lithium or Grignard reagents with elemental selenium followed by electrophilic alkylation. Alternatively, acetylides of these metals may be treated directly with electrophilic organoselenium species (diselenides or selenyl halides) [route (B)]. In a similar manner (hydrolytically sensitive) alkynyltrimethylstannanes react with organoselenyl chloride with elimination of SnMe₃Cl.³ Finally, selenolates react with (potentially explosive) bromoalkynes to afford alkynyl selenoethers.³

We report herein a new route to alkynyl selenoethers (Scheme 2) employing readily available bis(alkynyl)mercurials. Notwithstanding the toxicity of organomercurials, this approach offers some practical advantages, including high yields, easy purification of precursors and products, and the use of aerobic conditions. The precursor bis(alkynyl)mercurials are crystalline air- and moisture-stable reagents. This obviates the need for the assay of lithium or Grignard reagents, required in alternative procedures. The present method is therefore particularly convenient for small-scale preparations.

Bis(alkynyl)mercurials have been used for the transfer of acetylde groups to transition metals, often under very mild conditions.¹¹⁻¹⁴ In practical terms these reagents offer a number of advantages over other main group metal acetylides: their preparation is trivial (Scheme 2)^{15,16} and normally proceeds in very high yields. Indeed, in earlier times the formation of such compounds was a routine method for the characterisation of terminal alkynes.¹⁶ They are in general crystalline compounds with high thermal and aerobic stability in contrast to hydrolytic-



Scheme 1 X = Cl, Br or I; M = Li, or MgX

ally sensitive alkynylstannanes and air-sensitive copper acetylides. Their deployment in the synthesis of alkynyl derivatives of selenium therefore appeared attractive.

Results and Discussion

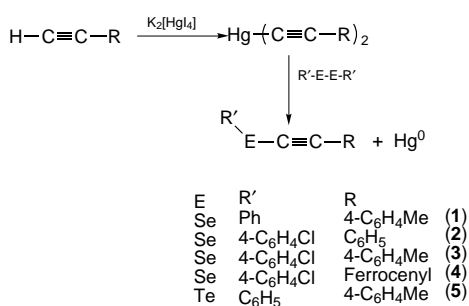
Our approach follows from early observations that dialkylmercurials react with diaryl diselenides to provide aryl alkyl selenides and elemental mercury (Scheme 3).¹⁷ Notably, this reaction fails for diarylmercurials, however we find that heating bis(4-tolyethynyl)mercury in refluxing toluene with 1 equivalent of diphenyl diselenide leads to smooth deposition of elemental mercury over 3 d. On removal of mercury and work-up, the product of the reaction was found to be phenyl 4-tolyethynyl selenide **1** (70% yield). The reaction was extended to include the derivatives shown in Scheme 2. These include the unusual ferrocenylethynyl derivative **4** which results in high yield from the reaction of bis(ferrocenylethynyl)mercury and di(4-chlorophenyl) diselenide.

The approach has also been extended to include the synthesis of phenyl 4-tolyethynyl telluride **5** in 72% yield. Electrophilic sources of divalent tellurium ('R-Te-X') remain scarce or ill defined limiting their use in the alkynyllithium/Grignard route (B). In contrast, diaryl ditellurides are conveniently and generally accessible. To date the method of choice for the formation of alkynyl telluroethers has been the alkylation of alkali-metal alkynyl tellurides,¹⁸ and this approach has been extended to the synthesis of symmetrical bis(alkyltellenyl)ethynes.¹⁹ The approach is however clearly not appropriate to the synthesis of alkynes bearing aromatic substituents on tellurium, and the preparation of such compounds requires the use of halogenoalkynes.^{20,†}

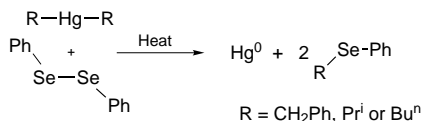
Two apparent limitations to our approach have emerged. (i) The reaction fails for diphenyl disulfide, although there seems no obvious reason for this. Fortunately, ample alternative strategies exist for the preparation of alkynyl thioethers. (ii) No alkynyl selenide could be obtained from the reaction of

[†] E-Mail: a.hill@ic.ac.uk

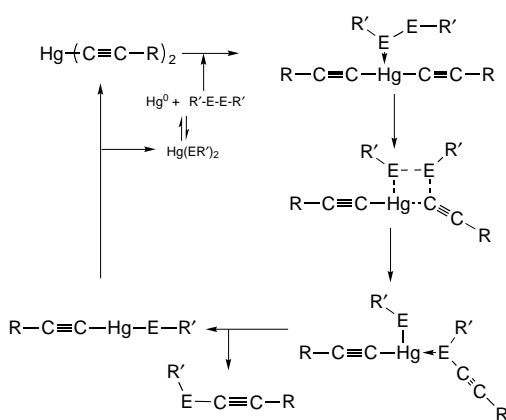
[‡] Very recently this approach has been extended to the reactions of alkynylidonium triflates with LiTePh.²¹



Scheme 2



Scheme 3 (ref. 15)



Scheme 4

diphenyl diselenide with bis(hex-1-ynyl)mercury, suggesting perhaps that either the approach is unsuitable for aliphatic alkynes, or that the aliphatic alkynyl selenides are unstable at the temperatures required for the exchange reaction. Finally, the process has only been demonstrated for one illustrative example of an alkynyl telluride. Although comparable yields were obtained compared to the selenium derivatives, the broader generality for tellurium has yet to be confirmed.

The mechanism of the formation of compounds 1–5 is complex and the progress of the reaction not readily amenable to monitoring. The process generates metallic mercury complicating *in situ* NMR measurements and the characteristic infrared absorptions due to the alkynyl group are neither strong nor particularly diagnostic. In the absence of kinetic data, we suspect the reaction proceeds *via* the steps shown in Scheme 4, *i.e.* (i) initial co-ordination of the diselenide to mercury, (ii) σ metathesis *via* a four-membered transition state, (iii) dissociation of aryl alkynyl selenide and repetition of the sequence to metathesise the remaining acetylide group {alternatively, symmetrisation of the mixed alkynylmercury selenolate could provide bis(alkynyl)mercury and [Hg(ER')₂] and (iv) thermal extrusion of mercury from [Hg(ER')₂] to provide diphenyl dichalcogenide for reintroduction into the sequence. This mechanism is supported by the following points. Bis(alkynyl)mercurials show limited Lewis acidity, forming adducts with *e.g.* bipyridyl and phenanthroline,²² supporting the proposed diselenide adduct formation. Many examples of organic group transfers from mercury to other elements have been suggested to proceed *via* four-centred σ -metathesis transition states.^{15,23} Finally, the insertion of mercury into diphenyl diselenide and the thermally induced extrusion of mercury from [Hg(SePh)₂]

have both been previously demonstrated,^{17,24} as has the insertion of mercury into the Te–Te bond of ditellurides.²⁵

Experimental

All operations were carried out under aerobic conditions. All solvents were used as received. Infrared spectra were recorded on a Perkin-Elmer 1720-X spectrometer, hydrogen-1 and carbon-13 NMR spectra in CDCl₃ on a JEOL EX270 spectrometer with chemical shifts reported in δ vs. SiMe₄ (¹H) or vs. internal CDCl₃ (¹³C δ 77.0). Departmental policy prevented us from obtaining elemental microanalytical data due to the involvement of mercury in the synthetic route, however accurate mass spectral data are given. Bis(alkynyl)mercurials were prepared by the general method outlined (Scheme 2)^{15,16} and recrystallised from chloroform and hexane. The diselenides and diphenyl ditelluride were obtained commercially.

Preparations

Phenyl 4-tolyethynyl selenide 1. Diphenyl diselenide (0.36 g, 1.2 mmol) and bis(4-tolyethynyl)mercury (0.50 g, 1.2 mmol) were suspended in toluene (20 cm³) and heated under reflux for 72 h. On cooling the solution was passed through diatomaceous earth and the filtrate freed of volatiles under reduced pressure. The residue was crystallised from a mixture of dichloromethane and hexane at –20 °C to provide pale yellow crystals. Yield 0.55 g (70%). IR: ν_{max} (Nujol) 2156 cm⁻¹. NMR (CDCl₃, 25 °C): ¹H, δ 2.31 (s, 3 H, CH₃), 7.10, 7.37 [(AB)₂, 4 H, $J(\text{AB}) = 8.1$ Hz, C₆H₄], 7.27, 7.54 (m \times 2, 5 H, C₆H₅); ¹³C-{¹H}, δ 138.8, 129.2, 126.9, 120.1 (1 C \times 4), 131.7, 129.5, 129.1, 128.8 (2 C \times 4), 103.2 (C \equiv CSe), 68.2 [C \equiv CSe, $J(\text{SeC}) = 180$ Hz] and 21.7 (CH₃). EI mass spectrum: $m/z = 272$ (M^+), 192 ([$M - \text{Se}$]⁺) and 115 ([$M - \text{SePh}$]⁺). Accurate mass spectrum: Found M^+ , m/z 272.0105. C₁₅H₁₂⁸⁰Se requires 272.0104.

4-Chlorophenyl phenylethynyl selenide 2. Bis(phenylethynyl)mercury (0.50 g, 1.2 mmol) and di(4-chlorophenyl) diselenide (0.47 g, 1.2 mmol) were suspended in toluene (20 cm³) and heated under reflux for 72 h. On cooling the solution was passed through diatomaceous earth and the filtrate freed of volatiles under reduced pressure. Recrystallisation of the residue from dichloromethane and hexane provided pale yellow crystals. Yield 0.59 g (82%). IR: ν_{max} (Nujol) 2161 cm⁻¹. NMR (CDCl₃, 25 °C): ¹H δ 7.33–7.37, 7.48–7.52 (m \times 2, 5 H, C₆H₅), 7.52, 7.31 [(AB)₂, 4 H, $J(\text{AB}) = 8.9$ Hz, C₆H₄]; ¹³C-{¹H}, δ 133.2, 129.8, 126.9, 122.8 (1 C \times 4), 130.3, 130.1, 129.6, 128.3 (2 C \times 4), 103.2 (C \equiv CSe) and 68.4 (C \equiv CSe). EI mass spectrum: $m/z = 292$ (M^+), 212 ([$M - \text{Se}$]⁺) and 176 ([$M - \text{Se} - \text{HCl}$]⁺). Accurate mass spectrum: Found M^+ , m/z 291.9545. C₁₄H₉³⁵Cl⁸⁰Se requires 291.9557.

4-Chlorophenyl 4-tolyethynyl selenide 3. Di(4-chlorophenyl) diselenide (0.95 g, 2.5 mmol) and bis(4-tolyethynyl)mercury (1.00 g, 2.5 mmol) were suspended in toluene (40 cm³) and heated under reflux for 72 h. On cooling the yellow solution was passed through diatomaceous earth to remove deposited mercury and the solvent removed under reduced pressure at 40 °C (rotary evaporator). The residue was crystallised from a mixture of dichloromethane and hexane at –20 °C to provide pale yellow crystals. Yield 1.12 g (79%). IR: ν_{max} (Nujol) 2161 cm⁻¹. NMR (CDCl₃, 25 °C): ¹H, δ 2.37 (s, 3 H, CH₃), 7.15, 7.30, 7.40, 7.51 [(AB)₂ \times 4, 8 H, $J(\text{AB}) \approx 8.0$ –8.6 Hz, C₆H₄Cl and C₆H₄Me]; ¹³C-{¹H}, δ 139.1, 133.2, 127.3, 119.8 (1 C \times 4), 131.8, 130.2, 129.6, 129.1 (2 C \times 4), 103.6 (C \equiv CSe), 67.6 (C \equiv CSe) and 21.6 (CH₃). EI mass spectrum: $m/z = 306$ (M^+), 226 ([$M - \text{Se}$]⁺), 189 ([$M - \text{Se} - \text{HCl}$]⁺) and 115 ([$M - \text{SeC}_6\text{H}_4\text{Cl}$]⁺). Accurate mass spectrum: Found M^+ , m/z 305.9745. C₁₅H₁₁³⁵Cl⁸⁰Se requires 305.9714.

4-Chlorophenyl ferrocenylethynyl selenide 4. A suspension of bis(ferrocenylethynyl)mercury (0.20 g, 0.30 mmol) and di(4-chlorophenyl) diselenide (0.13 g, 0.30 mmol) in toluene (15 cm³) was heated under reflux for 72 h. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (10 cm³). The orange-brown extract was chromatographed on silica gel, eluting with diethyl ether. The initial orange fraction was collected, concentrated and cooled to provide orange crystals. Yield 0.21 g (81%). NMR (CDCl₃, 25 °C): ¹H, δ 4.24 (s, 5 H, C₅H₅), 4.27, 4.52 [vt × 2, 4 H, C₅H₄, J(HH) ≈ 2], 7.30, 7.50 [(AB)₂, 4 H, J(AB) = 8.6 Hz, C₆H₄]; ¹³C-¹H, δ 133.0, 127.8 (1 C × 2), 130.0, 129.6 (2 C × 2), 103.2 (C≡CSe), 72.4, 69.5 (C²⁻⁵ of C₅H₄), 70.2 (C₅H₅), 64.3, 63.7 (C¹ of C₅H₄ and C≡CSe). EI mass spectrum: *m/z* = 400 (*M*⁺) and 320 ([*M* - Se]⁺). FAB mass spectrum: *m/z* = 799 (*M*₂⁺), 400 (*M*⁺), 320 ([*M* - Se]⁺) and 210 ([*M* - SeC₆H₄Cl]⁺). Accurate mass spectrum: Found *M*⁺, *m/z* 399.9238. C₁₈H₁₃³⁵Cl⁵⁶Fe⁸⁰Se requires 399.9220.

Phenyl 4-tolyethynyl telluride 5. A suspension of diphenyl ditelluride (0.28 g, 0.70 mmol) and bis(4-tolyethynyl)mercury (0.30 g, 0.70 mmol) in toluene (30 cm³) was heated under reflux for 72 h. The cooled solution was filtered through diatomaceous earth and the filtrate freed of volatiles under reduced pressure. The residue was crystallised from a mixture of dichloromethane and hexane to provide orange crystals. Yield 0.32 g (72%). IR: *v*_{max}(Nujol) 2140 cm⁻¹. NMR (CDCl₃, 25 °C): ¹H, δ 2.38 (s, 3 H, CH₃), 7.15, 7.39 [(AB)₂, 4 H, J(AB) = 8.1 Hz, C₆H₄], 7.30, 7.75 (m × 2, 5 H, C₆H₅); ¹³C-¹H, δ 138.9, 127.9, 120.4, 114.5 (1 C × 4), 135.1, 132.0, 129.8, 129.1 (2 C × 4), 106.2 (C≡CTe), 46.3 (C≡CTe) and 21.7 (CH₃). EI mass spectrum: *m/z* = 322 (*M*⁺), 245 ([*M* - Ph]⁺), 192 ([*M* - Te]⁺) and 115 ([*M* - TePh]⁺). Accurate mass spectrum: Found *M*⁺, *m/z* 321.9991. C₁₅H₁₂¹³⁰Te requires 322.0008.

Acknowledgements

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References

- 1 D. C. Miller and R. J. Angelici, *Organometallics*, 1991, **10**, 79, 89.
- 2 M. Plate, K. Dehnicke, S. Abram and U. Abram, *Z. Naturforsch., Teil B*, 1996, **51**, 1049.

- 3 H. Lang, H. Keller, W. Imhof and S. Martin, *Chem. Ber.*, 1990, **123**, 417.
- 4 A. F. Hill and J. M. Malget, *Chem. Commun.*, 1997, 2049.
- 5 J. V. Comasseto, V. Catani, J. T. B. Ferreira and A. L. Braga, *J. Chem. Soc., Chem. Commun.*, 1986, 1067; A. L. Braga, J. V. Comasseto and N. Petragnani, *Synthesis*, 1984, 240.
- 6 L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 1964, **83**, 307.
- 7 J. V. Comasseto, J. T. B. Ferreira and N. Petragnani, *J. Organomet. Chem.*, 1981, **216**, 287; J. V. Comasseto, *J. Organomet. Chem.*, 1983, **253**, 131.
- 8 S. Saito, S. Hamano, M. Iuaba and T. Moriwake, *Synth. Commun.*, 1984, **14**, 1105.
- 9 S. Raucher, M. R. Hansen and M. A. Colter, *J. Org. Chem.*, 1978, **43**, 4885.
- 10 I. Lalezari, *Synthesis*, 1984, 660.
- 11 J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, 1967, **89**, 844.
- 12 R. J. Cross and M. F. Davidson, *J. Chem. Soc., Dalton Trans.*, 1986, 411, 1987; R. J. Cross and J. Gemmill, *J. Chem. Soc., Dalton Trans.*, 1984, 199, 205.
- 13 D. M. McEwan, P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 1241.
- 14 R. B. Bedford, A. F. Hill, A. R. Thompsett, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1996, 1059.
- 15 L. G. Makarova and A. N. Nesmeyanov, *Methods of Elemento-organic Chemistry*, eds. A. N. Nesmeyanov and K. A. Kocheshkov, North-Holland, Amsterdam, 1967, vol. 4.
- 16 J. R. Johnson and W. L. McEwan, *J. Am. Chem. Soc.*, 1926, **48**, 469.
- 17 Y. Okamoto and T. Yano, *J. Organomet. Chem.*, 1971, **21**, 99.
- 18 J. L. Piette and M. Renson, *Bull. Soc. Chim. Belg.*, 1970, **79**, 353, 367, 383; M. J. Dabdoub and J. V. Comasseto, *Organometallics*, 1988, **7**, 84; L. Brandsma and H. E. Wijers, *Recl. Trav. Chim. Pays-Bas*, 1962, **81**, 583; Yu.-A. Boiko, B. S. Kupin and A. A. Petrov, *Zh. Org. Khim.*, 1969, **5**, 1553; A. A. Petrov, S. I. Radchenko, K. S. Mingaleva, I. G. Savich and V. B. Lebedev, *Zh. Obshch. Chim.*, 1964, **343**, 1899; S. I. Radchenko and A. A. Petrov, *Zh. Org. Khim.*, 1965, **1**, 2115; Yu.-A. Boiko, B. S. Kupin and A. A. Petrov, *Zh. Org. Khim.*, 1968, **4**, 1355.
- 19 R. W. Geldridge, jun., K. T. Higa, D. C. Harris, R. A. Nissan and M. P. Nadler, *Organometallics*, 1989, **8**, 2812.
- 20 M. J. Dabdoub, J. V. Comasseto and A. L. Braga, *Synth. Commun.*, 1988, **18**, 1979.
- 21 P. J. Stang and P. Murch, *Synthesis*, 1997, 1378.
- 22 M. Cano-Esquivel, A. Santos-Macias and I. Ballester-Reventos, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1153.
- 23 J. L. Wardell, in *Comprehensive Organometallic Chemistry*, 1st edn, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, 1982, vol. 2; A. G. Davies and J. L. Wardell, in *Comprehensive Organometallic Chemistry II*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, 1996, vol. 3.
- 24 A. Fredga, *Chem. Ber.*, 1938, **71**, 286.
- 25 J. Kischkewitz and D. Naumann, *Z. Anorg. Allg. Chem.*, 1987, **152**, 167.

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