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Synthesis of 1-alkynyl(diphenyl)onium salts of group 16 elements *via* heteroatom transfer reaction of 1-alkynyl(phenyl)-λ^3-iodanes

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Received 17th December 2002, Accepted 6th March 2003
First published as an Advance Article on the web 27th March 2003

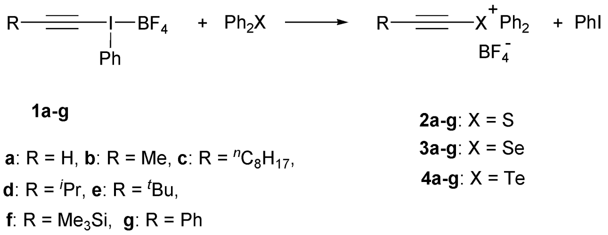
1-Alkynyl(phenyl)-λ^3-iodanes undergo selective transfer of the alkynyl groups over the phenyl group onto diphenyl chalcogens. Exposure of 1-alkynyl(phenyl)-λ^3-iodanes to diphenyl chalcogens (S, Se, and Te) in dichloromethane or 1,2-dichloroethane affords 1-alkynyl(diphenyl)sulfonium, -selenonium, and -telluronium salts in high yields.

Introduction

Efficient methods available for the synthesis of 1-alkynyl(aryl)onium salts of group 15 and 16 elements are limited. In 1987 we reported that the heteroatom transfer reaction between 1-alkynyl(phenyl)-λ^3-iodanes and triphenylphosphine provides a useful tool for the synthesis of 1-alkynyl(triphenyl)phosphonium salts.[1] The method was applied for the synthesis of 1-alkynyl(triphenyl)arsonium salts, but not for that of 1-alkynyl(triphenyl)stibonium and -bismuthonium salts,[2] probably because of the low nucleophilicity of triphenylstibine and triphenylbismuthine compared to triphenylphosphine and triphenylarsine.[3]

Silane–, germane–, stannane–, or borane–hypervalent λ^3-iodane exchange in the presence of a Lewis acid provides an efficient route for the synthesis of 1-alkynyl(aryl)-λ^3-iodanes: thus, reaction of alkynyl(trimethyl)silane with iodosylbenzene in the presence of BF_3–Et_2O affords alkynyl(phenyl)-λ^3-iodanes in high yields under mild conditions.[1,4] The exchange reaction was applied to the synthesis of alkynyl(diphenyl)selenonium and -telluronium salts:[5] diphenyl(phenylethynyl)selenonium or -telluronium salt was prepared by the Si–Se(IV) exchange reaction of (phenylethynyl)trimethylsilane with diphenyl selenoxide in the presence of trifluoromethanesulfonic anhydride or by the BF_3-promoted ligand exchange of (phenylethynyl)tributylstannane with diphenyltellurinyl difluoride, respectively.

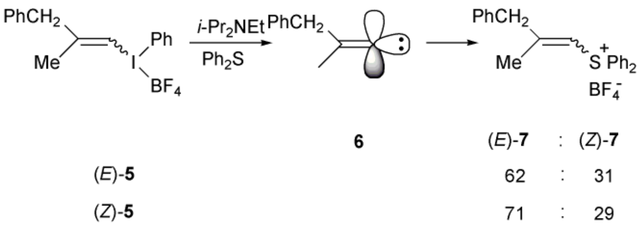
Herein, we report a general method for the synthesis of 1-alkynyl(diphenyl)sulfonium **2**, -selenonium **3**, and -telluronium salts **4**, which involves a heteroatom transfer reaction between 1-alkynyl(phenyl)-λ^3-iodanes **1** and diphenyl chalcogens under mild conditions (Scheme 1). In this reaction, the 1-alkynyl group of the λ^3-iodanes **1** was selectively transferred to the chalcogen atoms in preference to the phenyl group.



Scheme 1

Results and discussion

Diphenyl-λ^3-iodane (Ph_2IBF_4), on heating at 185 °C without using a solvent, undergoes oxidative phenyl group transfer to diphenyl sulfide to give triphenylsulfonium tetrafluoroborate with reductive elimination of iodobenzene.[6] Use of a catalytic amount of Cu(I) or Cu(II) salts accelerates the phenyl transfer reaction to such an extent that the reaction proceeds at temperatures as low as 120–130 °C.[7] Photochemical reaction of diphenyl-λ^3-iodanes with diphenyl sulfide in acetonitrile at room temperature results in the formation of triphenylsulfonium salts through a single electron transfer process.[8] The alkenyl group in (*E*)- and (*Z*)-1-alkenyl(phenyl)-λ^3-iodanes **5** was selectively transferred to diphenyl sulfide by the reaction with diisopropylethylamine to give a mixture of stereoisomers of alkenyl(diphenyl)sulfonium tetrafluoroborate **7**.[9] The involvement of free alkylidene carbene **6** *via* base-induced reductive α-elimination of **5** was firmly established by the high degree of stereoconvergence of the olefin geometry in this alkenyl transfer reaction (Scheme 2).



Scheme 2

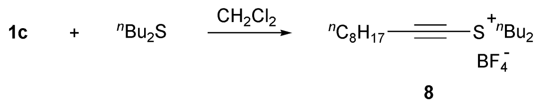
The results of alkynyl transfer reactions between 1-alkynyl(phenyl)-λ^3-iodanes **1**[4] and diphenyl chalcogens are summarized in Table 1. Exposure of 1-decynyl(phenyl)-λ^3-iodane **1c** to diphenyl sulfide in dichloromethane at room temperature for 48 h showed no evidence for an alkynyl transfer reaction; however, when a solution of **1c** and diphenyl sulfide (1.2 equiv) in 1,2-dichloroethane was heated at 83 °C for 26 h, the 1-decynyl group of **1c** was selectively transferred to diphenyl sulfide, and 1-decynyl(diphenyl)sulfonium tetrafluoroborate **2c** was obtained in 90% yield (Entry 7). Reaction times required for the alkynyl transfer in 1,2-dichloroethane at 83 °C depend on the differences in the steric demands of the alkyl substituents (R) attached to the acetylenic carbon atom in **1** and increase in the order of increasing steric hindrance: Me (**1b**, 12 h) < $^nC_8H_{17}$ (**1c**, 26 h) < ^{i}Pr (**1d**, 45 h) < ^{t}Bu (**1e**, 168 h) (Entries 4, 7, 12, and 15). Ethynylation of diphenyl sulfide with the least sterically demanding ethynyl-λ^3-iodane **1a** takes place at room temperature in dichloromethane (3 h). Phenylethynyl-λ^3-iodane **1g** also undergoes transfer of the phenylethynyl group to diphenyl sulfide without heating (Entry 20). Alkylation of the more nucleophilic dialkyl sulfide occurs smoothly; thus, the reaction of dibutyl sulfide with **1c** afforded the alkynylsulfonium salt **8** at room temperature (2.5 h) quantitatively (Scheme 3).

DOI: 10.1039/b212512a

Table 1 Alkynyl transfer reaction between 1-alkynyl(phenyl)-λ^3-iodanes **1** and diphenyl chalcogens[a]

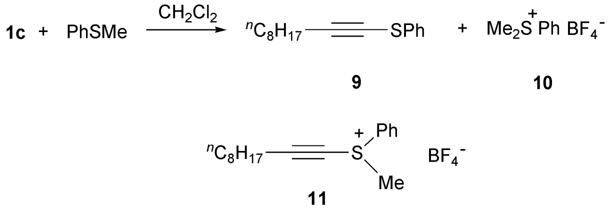
Entry	λ^3-Iodane **1**	Ph_2X[b]	Conditions Temp./°C	 Time/h	Product (Yield, %)[c]
1	**1a**	Ph_2S	25	1	**2a** (100)
2	**1a**	Ph_2Se	25	2	**3a** (96)
3	**1a**	Ph_2Te	25	3.5	**4a** (90)
4	**1b**	Ph_2S[d]	83	12	**2b** (83)
5	**1b**	Ph_2Se	40	15.5	**3b** (86)
6	**1b**	Ph_2Te	25	0.5	**4b** (91)
7	**1c**	Ph_2S[d]	83	26	**2c** (90)
8	**1c**	Ph_2Se	25	48	**3c** (30)[e]
9	**1c**	Ph_2Se	40	29	**3c** (86)
10	**1c**	Ph_2Se[d]	83	2	**3c** (98)
11	**1c**	Ph_2Te	25	3	**4c** (100)
12	**1d**	Ph_2S[d]	83	45	**2d** (66)
13	**1d**	Ph_2Se[d]	83	12	**3d** (78)
14	**1d**	Ph_2Te	25	5	**4d** (85)
15	**1e**	Ph_2S[d]	83	168	**2e** (56)
16	**1e**	Ph_2Se[d]	83	88	**3e** (93)
17	**1e**	Ph_2Te	25	3	**4e** (98)
18	**1f**	Ph_2Se[f]	25	39	**3f** (89)[e]
19	**1f**	Ph_2Te	25	2	**4f** (100)
20	**1g**	Ph_2S	25	19	**2g** (89)
21	**1g**	Ph_2Se	25	34	**3g** (85)
22	**1g**	Ph_2Te	25	2	**4g** (87)

[a] Reactions were carried out in dichloromethane under nitrogen, unless otherwise noted. [b] 1.2 equiv of Ph_2X were used. [c] Isolated yields. [d] 1,2-Dichloroethane was used as a solvent. [e] Yields were determined by ^1H NMR. [f] 5 equiv of Ph_2Se were used.



Scheme 3

The attempted direct alkynylation of thioanisole was accompanied by further methyl transfer reaction of the resulting alkynylsulfonium salt **11**; thus, treatment of **1c** with thioanisole (2.5 equiv) in dichloromethane at 40 °C gave a mixture of 1-decynyl phenyl sulfide **9** (88%) and dimethyl(phenyl)sulfonium tetrafluoroborate **10** (95%) (Scheme 4). Nucleophilic attack of thioanisole on the initially formed decynyl(methyl)(phenyl)sulfonium salt **11** probably transfers the methyl group to thioanisole and produces the sulfonium salt **10** with formation of the sulfide **9**.[10] Because of the decreased nucleophilicity of the sulfide **9** relative to thioanisole, the reverse methyl transfer from **10** to **9** will not take place under the conditions.

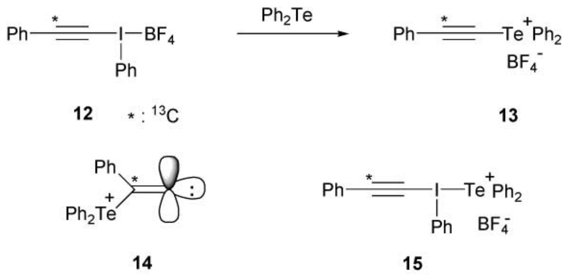


Scheme 4

No transfer reaction between the alkynyl-λ^3-iodanes **1** and oxygen nucleophiles was observed; even under prolonged heating in 1,2-dichloroethane, large amounts of the λ^3-iodane **1c** and diphenyl ether were recovered unchanged. This is probably due to the low nucleophilicity of diphenyl ether compared to diphenyl sulfide. More nucleophilic diphenyl selenide and telluride react with the alkynyl-λ^3-iodanes **1** under mild conditions to give the alkynylselenonium **3** and -telluronium salts **4** in high yields (Table 1); for instance, even the reaction of diphenyl telluride with the bulky 3,3-dimethyl-1-butynyl-λ^3-iodane **1e** takes place at room temperature. The rate of alkynyl transfer of **1** to diphenyl selenide also decreases with increasing steric demand of the alkynyl group in the order MeCC (**1b**) > $^nC_8H_{17}CC$ (**1c**) > ^iPrCC (**1d**) > ^tBuCC (**1e**) (Entries 5, 9, 10, 13, and 16). Thus, our 1-alkynyl transfer reaction provides an efficient route for the synthesis of 1-alkynyl(diphenyl)sulfonium **2**, -selenonium **3** and -telluronium salts **4**.

Because of the powerful electron-withdrawing nature of the phenyl-λ^3-iodanyl group $Ph(BF_4)I$— with a large Hammett substituent constant (σ_p: 1.37),[11] alkynyl-λ^3-iodanes **1** are highly electron-deficient species.[12] They act as good Michael acceptors toward a variety of soft nucleophiles, including stable enolates of 1,3-dicarbonyl compounds, oxygen (carboxylate and phenoxide), nitrogen (azide and amide), sulfur (sulfinate and thiocyanate) and halide nucleophiles.[13] Michael addition of diphenyl chalcogens to the β-carbons of alkynyl-λ^3-iodanes **1**, followed by reductive elimination of iodobenzene, will generate alkylidene carbenes. A subsequent 1,2-shift in the alkylidene carbenes results in the formation of the alkynyl(diphenyl)onium salts **2**–**4**. This mechanism explains both formation of the onium salts **2**–**4** and the relative rates of the transfer reaction that decrease in the order of Me (**1b**) > $^nC_8H_{17}$ (**1c**) > ^iPr (**1d**) > ^tBu (**1e**). Michael attack of diphenyl chalcogens on alkynyl-λ^3-iodanes **1** will be inhibited by a sterically demanding alkyl group (R) at the β-position, which slows down the rate of the alkynyl transfer reaction.

To gain some insight into the mechanism of this transfer reaction, phenyl(phenylethynyl-*2*-^{13}C)-λ^3-iodane **12** (99% enriched)[13a] was synthesized and subjected to the alkynyl transfer reaction with diphenyl telluride (Scheme 5). The ^{13}C enrichment at the β-acetylenic carbon of the resulting (phenylethynyl)telluronium salt **13** was found to be greater than 98% from the ^{13}C NMR spectrum. The reaction with diphenyl selenide gave a similar result, *i.e.* ^{13}C enrichment of more than 95% at the β-acetylenic carbon of the resulting (phenylethynyl)selenonium tetrafluoroborate. The well-known high migratory aptitude of α-aryl groups in alkylidene carbenes[13a,e] seems to suggest that the tandem Michael–alkylidene carbene mechanism involving generation of the reactive intermediate **14** may result in the predominant formation of the (phenylethynyl-*1*-^{13}C)telluronium salt through a facile 1,2-phenyl shift, instead of affording **13**. Although there is no experimental and theoretical evidence, it seems reasonable to assume that the migratory aptitude of the positively charged diphenyltelluronium group to the electron-deficient carbenic centre may be lower than that of the phenyl group.



Scheme 5

An alternative ligand coupling mechanism on iodine(III) of the telluronium salt **15**, produced by ligand exchange *via* the nucleophilic attack of diphenyl telluride at the positively charged iodine of **12**, may account for the selective formation of the telluronium salt **13**. A similar mechanism has been proposed for the reaction of alkynyl(phenyl)-λ^3-iodanes **1** with triphenylarsine.[2]

Whatever the mechanism, the method is attractive from the practical standpoint, because of its mildness, cleanliness, and the ease with which the alkynyl(diphenyl)onium salts **2**–**4** can be isolated. The results presented suggest that the alkynyl transfer reaction between 1-alkynyl(phenyl)-λ^3-iodanes **1** and diphenyl chalcogens takes place selectively under mild conditions.

Experimental

General

IR spectra were recorded on JASCO IRA-1 and Perkin Elmer 1720 FT-IR spectrometers. ^{1}H and ^{13}C NMR were recorded on JEOL FX-200 and JMN-GCX 400 spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from internal Me_4Si. Mass spectra (MS) were obtained on a JEOL JMS-DX300 spectrometer. Melting points were determined with a Yanaco micro melting points apparatus and are uncorrected. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Dichloromethane and 1,2-dichloroethane were dried over CaH_2 and distilled under nitrogen. Diphenyl sulfide and selenide, dibutyl sulfide and thioanisole are commercially available. Diphenyl telluride was prepared according to the reported method.[14] 1-Alkynyl(phenyl)-λ^3-iodanes **1** and **12** were prepared from the corresponding 1-alkynyl(trimethyl)silanes by reaction with iodosylbenzene in the presence of BF_3–Et_2O in dichloromethane according to the literature procedure.[4]

General procedure for synthesis of 1-alkynyl(diphenyl)onium tetrafluoroborates 2–4. To a stirred solution of a 1-alkynyl(phenyl)-λ^3-iodane **1** (0.2 mmol) in 2 cm^3 of dichloromethane or 1,2-dichloroethane was added a diphenyl chalcogen (0.24 mmol) under nitrogen, and the solution was stirred under the conditions shown in Table 1. The solvent was evaporated under reduced pressure to give an oil, which was washed several times with dichloromethane–hexane or –diethyl ether by decantation at −78 °C to give 1-alkynyl(diphenyl)onium salt **2**–**4**. Yields of the products are given in Table 1.

Diphenyl(ethynyl)sulfonium tetrafluoroborate 2a. Pale yellow oil {HRMS (FAB) Calc. for $C_{14}H_{11}S$: ([M − BF_4]$^+$), 211.0582. Found: *m*/*z*, 211.0597}; ν_{max} (neat)/cm^{-1} 3222, 3095, 2076, 1616, 1448, 1150–1000, 748 and 682; δ_H (400 MHz; $CDCl_3$) 8.13 (4 H, d, *J* 7.3), 7.78 (2 H, t, *J* 7.3), 7.72 (4 H, t, *J* 7.3) and 4.54 (1 H, s).

Diphenyl(1-propynyl)sulfonium tetrafluoroborate 2b. Colourless needles (from dichloromethane–hexane); mp 127–129 °C {Found: C, 57.69, H, 4.43%; HRMS (FAB), 225.0747. Calc. for $C_{15}H_{13}BF_4S$: C, 57.71; H, 4.20%; [M − BF_4]$^+$, 225.0738}; ν_{max} (nujol)/cm^{-1} 3222, 2210, 1460, 1435, 1150–1000, 740 and 675; δ_H (200 MHz; $CDCl_3$) 8.20–8.00 (4 H, m), 7.80–7.48 (6 H, m) and 2.43 (3 H, s); δ_C (100 MHz; $CDCl_3$) 134.8, 131.7, 129.3, 127.7, 113.9, 53.0 and 5.9.

1-Decynyl(diphenyl)sulfonium tetrafluoroborate 2c. Oil {HRMS (FAB) Calc. for $C_{22}H_{27}S$: ([M − BF_4]$^+$), 323.1833. Found: *m*/*z*, 323.1865}; ν_{max} (neat)/cm^{-1} 2910, 2205, 1440, 1150–1000, 750 and 680; δ_H (200 MHz; $CDCl_3$) 8.20–8.02 (4 H, m), 7.72–7.60 (6 H, m), 2.78 (2 H, t, *J* 7.2), 1.73 (2 H, quint, *J* 7.2), 1.54–1.05 (10 H, m) and 0.86 (3 H, t, *J* 6.6); δ_C (100 MHz; $CDCl_3$) 134.8, 131.7, 129.3, 127.9, 117.3, 54.2, 31.6, 29.0, 28.9, 28.8, 27.0, 22.5, 20.5 and 14.0.

Diphenyl(3-methyl-1-butynyl)sulfonium tetrafluoroborate 2d. Colourless needles (from dichloromethane–hexane); mp 153–156 °C {HRMS (FAB) Calc. for $C_{17}H_{17}S$: ([M − BF_4]$^+$), 253.1051. Found: *m*/*z*, 253.1059}; ν_{max} (nujol)/cm^{-1} 2970, 2200, 1450, 1150–1000, 770 and 690; δ_H (200 MHz; $CDCl_3$) 8.16–8.04 (4 H, m), 7.76–7.60 (6 H, m), 3.13 (1 H, sept, *J* 6.8) and 1.39 (6 H, d, *J* 6.8); δ_C (100 MHz; $CDCl_3$) 134.8, 131.8, 129.3, 127.8, 120.9, 54.0, 22.4 and 21.1.

3,3-Dimethyl-1-butynyl(diphenyl)sulfonium tetrafluoroborate 2e. Colourless needles (from dichloromethane–diethyl ether); mp 144–145 °C {Found: C, 60.58, H, 5.25%; HRMS (FAB), 267.1211. Calc. for $C_{18}H_{19}BF_4S\cdot\frac{1}{4}H_2O$: C, 60.27; H, 5.48%; [M − BF_4]$^+$, 267.1207}; ν_{max} (nujol)/cm^{-1} 2975, 2200, 1450, 1150–1000, 750 and 690; δ_H (200 MHz; $CDCl_3$) 8.18–8.06 (4 H, m), 7.76–7.64 (6 H, m) and 1.45 (9 H, s).

Diphenyl(phenylethynyl)sulfonium tetrafluoroborate 2g. Reddish oil {HRMS (FAB) Calc. for $C_{20}H_{15}S$: ([M − BF_4]$^+$), 287.0894. Found: *m*/*z*, 287.0893}; ν_{max} (neat)/cm^{-1} 2184, 1474, 1446, 1150–1000, 754 and 685; δ_H (400 MHz; $CDCl_3$) 8.17 (4 H, d, *J* 7.5), 7.81 (2 H, d, *J* 7.7), 7.77–7.64 (6 H, m), 7.60 (1 H, t, *J* 7.4) and 7.48 (2 H, dd, *J* 7.7 and 7.4).

Diphenyl(ethynyl)selenonium tetrafluoroborate 3a. Oil {HRMS (FAB) Calc. for $C_{14}H_{11}Se$: ([M − BF_4]$^+$, ^{80}Se), 259.0026. Found: *m*/*z*, 259.0005}; ν_{max} (neat)/cm^{-1} 3231, 3064, 2063, 1476, 1446, 1150–1000, 743 and 682; δ_H (400 MHz; CD_3OD) 7.94 (4 H, d, *J* 7.5), 7.64–7.75 (6 H, m) and 4.92 (1 H, s). Selenonium salt **3a** is labile and contaminated with a small amount of impurity.

Diphenyl(1-propynyl)selenonium tetrafluoroborate 3b. Colourless leaflets (from dichloromethane–hexane); mp 184–186 °C {Found: C, 49.83, H, 3.76%; HRMS (FAB), 273.0172. Calc. for $C_{15}H_{13}BF_4Se$: C, 50.18; H, 3.65%; [M − BF_4]$^+$, ^{80}Se, 273.0182}; ν_{max} (KBr)/cm^{-1} 3048, 2204, 1567, 1441, 1150–1000, 739 and 680; δ_H (200 MHz; CD_3OD) 8.0–7.9 (4 H, m), 7.72–7.6 (6 H, m) and 2.35 (3 H, s); δ_C (100 MHz; $CDCl_3$) 134.4, 133.3, 132.5, 130.9, 110.8, 56.6 and 5.1.

1-Decynyl(diphenyl)selenonium tetrafluoroborate 3c. Oil {HRMS (FAB) Calc. for $C_{22}H_{27}Se$: ([M − BF_4]$^+$, ^{80}Se), 371.1264. Found: *m*/*z*, 371.1279}; ν_{max} (nujol)/cm^{-1} 2920, 2190, 1440, 1150–1000 and 745; δ_H (200 MHz; $CDCl_3$) 8.0–7.9 (4 H, m), 7.65–7.54 (6 H, m), 2.67 (2 H, t, *J* 7.5), 1.70 (2 H, quint, *J* 7.5), 1.5–1.1 (10 H, m) and 0.88 (3 H, t, *J* 6.6); δ_C (100 MHz; $CDCl_3$) 133.5, 131.5, 130.1, 129.4, 116.1, 54.2, 31.6, 28.9, 28.7, 28.7, 27.2, 22.5, 20.2 and 13.9.

Diphenyl(3-methyl-1-butynyl)selenonium tetrafluoroborate 3d. Colourless needles (from dichloromethane–hexane); mp 137–141 °C {HRMS (FAB) Calc. for $C_{17}H_{17}Se$: ([M − BF_4]$^+$, ^{80}Se), 301.0495. Found: *m*/*z*, 301.0508}; ν_{max} (nujol)/cm^{-1} 2960, 2190, 1450, 1160–1000, 750 and 680; δ_H (200 MHz; $CDCl_3$) 8.00–7.85 (4 H, m), 7.70–7.54 (6 H, m), 3.03 (1 H, sept, *J* 7.0) and 1.37 (6 H, d, *J* 7.0); δ_C (100 MHz; $CDCl_3$) 133.5, 131.5, 130.1, 129.5, 120.2, 54.2, 22.3 and 21.5.

3,3-Dimethyl-1-butynyl(diphenyl)selenonium tetrafluoroborate 3e. Colourless prisms (from dichloromethane–hexane); mp 178–182 °C {HRMS (FAB) Calc. for $C_{18}H_{19}Se$: ([M − BF_4]$^+$, ^{80}Se), 315.0652. Found: *m*/*z*, 315.0628}; ν_{max} (nujol)/cm^{-1} 2960, 2200, 2170, 1445, 1160–1100, 750 and 680; δ_H (200 MHz; $CDCl_3$) 8.04–7.88 (4 H, m), 7.72–7.52 (6 H, m) and 1.43 (9 H, s); δ_C (100 MHz; $CDCl_3$) 133.5, 131.5, 130.2, 129.4, 122.6, 53.9, 29.9 and 29.6.

Diphenyl(trimethylsilylethynyl)selenonium tetrafluoroborate 3f. Oil {HRMS (FAB) Calc. for $C_{17}H_{19}SeSi$: ([M − BF_4]$^+$, ^{80}Se), 331.0421. Found: *m*/*z*, 331.0428}; ν_{max} (neat)/cm^{-1} 3036, 2064, 1477 and 1100–1000; δ_H (200 MHz; $CDCl_3$) 8.04–7.88 (4 H, m), 7.75–7.55 (6 H, m) and 0.37 (9 H, s). The onium salt **3f** is highly labile.

Diphenyl(phenylethynyl)selenonium tetrafluoroborate 3g.[5a] δ_C (100 MHz; $CDCl_3$) 133.6, 133.2, 132.4, 131.6, 130.1, 129.7, 129.0, 117.7, 111.0 and 63.4.

Diphenyl(ethynyl)telluronium tetrafluoroborate 4a. Colourless prisms (from dichloromethane–hexane); mp 153–157 °C; ν_{max} (KBr)/cm^{-1} 3247, 2048, 1909, 1440, 1150–1000, 734 and 685; δ_H (200 MHz; CD_3OD) 7.96–7.8 (4 H, m), 7.62–7.48 (6 H, m), 4.05 (1 H, s); FAB MS *m/z* 309 ([M − BF_4]$^+$, ^{130}Te, 100%), 307 ([M − BF_4]$^+$, ^{128}Te, 92), 305 ([M − BF_4]$^+$, ^{126}Te, 62).

Diphenyl(1-propynyl)telluronium tetrafluoroborate 4b. Colourless prisms (from dichloromethane–hexane); mp 222–225 °C {Found: C, 43.06, H, 3.19%; HRMS (FAB), 323.0060. Calc. for $C_{15}H_{13}BF_4Te\cdot\frac{1}{2}H_2O$: C, 43.24; H, 3.39%; [M − BF_4]$^+$, ^{130}Te, 323.0080}; ν_{max} (nujol)/cm^{-1} 2175, 1440, 1150–1000 and 735; δ_H (200 MHz; $CDCl_3$) 7.98 (4 H, br d, *J* 7.1), 7.64–7.53 (6 H, m) and 2.30 (3 H, s); δ_C (100 MHz; CD_3OD) 135.0, 133.0, 131.5, 129.8, 112.2, 58.5 and 4.9.

1-Decynyl(diphenyl)telluronium tetrafluoroborate 4c. Oil {HRMS (FAB) Calc. for $C_{22}H_{27}Te$: ([M − BF_4]$^+$, ^{130}Te), 421.1172. Found: *m/z*, 421.1176}; ν_{max} (neat)/cm^{-1} 2910, 2850, 2175, 1430, 1150–1000, 735 and 680; δ_H (200 MHz; $CDCl_3$) 8.2–7.9 (4 H, m), 7.62–7.45 (6 H, m), 2.59 (2 H, t, *J* 7.0), 1.65 (2 H, quint, *J* 7.0), 1.5–1.1 (10 H, m) and 0.87 (3 H, t, *J* 6.6); δ_C (100 MHz; $CDCl_3$) 133.8, 132.6, 131.0, 125.1, 120.5, 53.7, 31.7, 29.0, 28.8, 28.8, 27.6, 22.6, 20.6 and 14.0; FAB MS *m/z* 421 ([M − BF_4]$^+$, ^{130}Te, 100%), 419 ([M − BF_4]$^+$, ^{128}Te, 95), 417 ([M − BF_4]$^+$, ^{126}Te, 60).

Diphenyl(3-methyl-1-butynyl)telluronium tetrafluoroborate 4d. Colourless prisms (from dichloromethane–hexane); mp 134–138 °C{HRMS (FAB) Calc. for $C_{17}H_{17}Te$: ([M − BF_4]$^+$, ^{130}Te), 351.0393. Found: *m/z*, 351.0309}; ν_{max} (nujol)/cm^{-1} 2175, 1440, 1150–1000 and 740; δ_H (200 MHz; $CDCl_3$) 8.0–7.8 (4 H, m), 7.64–7.4 (6 H, m), 2.93 (1 H, sept, *J* 6.8) and 1.32 (6 H, d, *J* 6.8); δ_C (100 MHz; $CDCl_3$) 133.7, 132.6, 131.0, 125.4, 125.0, 52.6, 22.4 and 21.8; FAB MS *m/z* 351 ([M − BF_4]$^+$, ^{130}Te, 100%), 349 ([M − BF_4]$^+$, ^{128}Te, 87), 347 ([M − BF_4]$^+$, ^{126}Te, 70).

3,3-Dimethyl-1-butynyl(diphenyl)telluronium tetrafluoroborate 4e. Colourless prisms (from dichloromethane–hexane); mp 198–201 °C {Found: C, 42.32, H, 4.78%; HRMS (FAB), 365.0565. Calc. for $C_{18}H_{19}BF_4Te$: C, 42.51; H, 4.90%; [M − BF_4]$^+$, ^{130}Te, 365.0549}; ν_{max} (nujol)/cm^{-1} 2970, 2180, 2150, 1460, 1160–1000, 740 and 685; δ_H (200 MHz; $CDCl_3$) 8.0–7.85 (4 H, m), 7.6–7.44 (6 H, m) and 1.37 (9 H, s); δ_C (100 MHz; $CDCl_3$) 133.6, 132.6, 131.0, 128.0, 125.0, 52.1, 30.0 and 29.6; FAB MS *m/z* 365 ([M − BF_4]$^+$, ^{130}Te, 100%), 363 ([M − BF_4]$^+$, ^{128}Te, 93), 361 ([M − BF_4]$^+$, ^{126}Te, 59).

Diphenyl(trimethylsilylethynyl)telluronium tetrafluoroborate 4f. Pale yellow prisms (from dichloromethane–hexane); mp 112–114 °C{HRMS (FAB) Calc. for $C_{17}H_{19}SiTe$: ([M − BF_4]$^+$, ^{130}Te), 381.0318. Found: *m/z*, 381.0293}; ν_{max} (nujol)/cm^{-1} 2030, 2150, 1440, 1160–1000, 850, 740 and 690; δ_H (200 MHz; $CDCl_3$) 8.0–7.86 (4 H, m), 7.58–7.44 (6 H, m) and 0.30 (9 H, s); FAB MS *m/z* 381 ([M − BF_4]$^+$, ^{130}Te, 100%), 379 ([M − BF_4]$^+$, ^{128}Te, 94), 377 ([M − BF_4]$^+$, ^{126}Te, 64).

Diphenyl(phenylethynyl)telluronium tetrafluoroborate 4g.[5b] δ_C (100 MHz; $CDCl_3$) 134.0, 132.9, 132.5, 131.3, 131.0, 128.7, 125.6, 119.4, 115.1 and 63.7.

Reaction of 1-decynyl-λ^3-iodane 1c with dibutyl sulfide. To a stirred solution of 1-decynyl(phenyl)-λ^3-iodane **1c** (86 mg, 0.20 mmol) in dichloromethane (2 cm^3) was added dibutyl sulfide (35 mg, 0.24 mmol) under nitrogen at room temperature, and the solution was stirred for 2.5 h. The solvent was evaporated under reduced pressure to give an oil, which was washed several times with hexane by decantation at −78 °C to give 1-decynyl(dibutyl)sulfonium tetrafluoroborate **8** (74 mg, 100%) as a pale yellow oil. Compound **8**: {HRMS (FAB) Calc. for $C_{18}H_{35}S$: ([M − BF_4]$^+$), 283.2459. Found: *m/z*, 283.2495}; ν_{max} (nujol)/cm^{-1} 2925, 2220, 1470 and 1150–1000; δ_H (200 MHz; $CDCl_3$) 3.8–3.5 (4 H, m), 2.58 (2 H, t, *J* 7.0), 1.92 (4 H, quint, *J* = 7.0), 1.8–1.2 (16 H, m), 1.0 (6 H, t, *J* 7.0) and 0.88 (3 H, t, *J* 7.0); δ_C (100 MHz; $CDCl_3$) 111.8, 54.4, 46.4, 31.6, 29.0, 28.8, 28.7, 27.1, 26.6, 22.5, 21.1, 20.0, 13.9 and 13.3.

Reaction of 1-decynyl-λ^3-iodane 1c with thioanisole. To a stirred solution of 1-decynyl(phenyl)-λ^3-iodane **1c** (86 mg, 0.20 mmol) in dichloromethane (2 cm^3) was added thioanisole (62 mg, 0.50 mmol) under nitrogen at room temperature, and the solution was refluxed for 47 h. The solvent was evaporated under reduced pressure. Decantation of the reaction mixture with dichloromethane–hexane at −78 °C gave dimethyl(phenyl)sulfonium tetrafluoroborate **10** (43 mg, 95%). The organic solvent was evaporated under reduced pressure to give an oil, which was purified by preparative TLC to give 1-decynyl phenyl sulfide **9** (43.4 mg, 88%). Compound **9**: pale yellow oil {HRMS Calc. for $C_{16}H_{22}S$: *M*, 246.1427. Found: *m/z*, M$^+$, 246.1442}; ν_{max} ($CHCl_3$)/cm^{-1} 2925, 2180, 1465 and 1090; δ_H (200 MHz; $CDCl_3$) 7.45–7.10 (5 H, m), 2.44 (2 H, t, *J* 6.8), 1.7–1.1 (12 H, m) and 0.88 (3 H, t, *J* 6.8); *m/z* 246 (M$^+$, 45%), 141 (44), 125 (25), 95 (58), 81 (100). Salt **10**: Colourless prisms; mp 134–135 °C (from dichloromethane–hexane, lit.[15] mp 128–132 °C); δ_H (400 MHz; $CDCl_3$) 7.95 (2 H, br d, *J* 8.5), 7.81 (1 H, br t, *J* 7.7), 7.73 (2 H, br dd, *J* 8.5 and 7.7) and 3.37 (6 H, s).

Reaction of phenyl(phenylethynyl-*2*-^{13}*C*)-λ^3-iodane 12 with diphenyl telluride. To a stirred solution of phenyl(phenylethynyl-*2*-^{13}*C*)-λ^3-iodane **12** (99% enriched, 42 mg, 0.11 mmol)[13a] in dichloromethane (1.5 cm^3) was added diphenyl telluride (36 mg, 0.13 mmol) under nitrogen at room temperature, and the solution was stirred for 15 h. The solvent was evaporated under reduced pressure to give an oil, which was washed several times with dichloromethane–hexane by decantation at −78 °C to give a diphenyl(phenylethynyl-*2*-^{13}*C*)telluronium tetrafluoroborate **13** (40.8 mg, 82%) as a brown oil. ^{13}C NMR signals of C1, C2 and C3 of the telluronium salt **13** in $CDCl_3$ appear at δ 63.1 (d, J_{C1-C2} 158.1), 115.4 (s) and 119.4 (d, J_{C2-C3} 84.6) ppm and the ^{13}C enrichment at C2 of **13** was determined to be greater than 98%.

In a similar manner, the reaction of (phenylethynyl-*2*-^{13}*C*)-λ^3-iodane **12** with diphenyl selenide gave diphenyl(phenylethynyl-*2*-^{13}*C*)selenonium tetrafluoroborate (59%): δ_C (100 MHz; $CDCl_3$) 110.9 (s, C2) and 63.4 (d, J_{C1-C2} 180.1, C1). The ^{13}C enrichment at the C2 was determined to be greater than 95%.

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