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TETRAHEDRON

Synthesis of Ketene (S, Te)Acetals and Their Transformation into *Z*-α-Phenylthio-α,β-unsaturated Aldehydes

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Abstract: *Reaction of thiomethyl phosphonates with aryl (or butyl) tellurenyl halides and aldehydes under basic conditions provides moderate to good yields of ketene thio (telluro) acetals, with vinylic sulfides being byproducts of this transformation. Tellurium-lithium exchange by reaction with n-BuLi yielded vinyl organolithium species, which were captured with several electrophiles. In the case of DMF, Z-α-phenylthio-α,β-unsaturated aldehydes were obtained.*

Keywords: Wittig reactions; Sulfides; Aldehydes; Ketenes

INTRODUCTION

Vinylic tellurides have recently attracted considerable attention as important synthetic reagents and intermediates,[1] especially in transmetalation reactions. In addition, vinylic sulfides[2] and selenides[1] have already been recognized as useful intermediates for several processes in organic synthesis.

We have recently described practical methodologies for the preparation of vinylic sulfides,[3] selenides,[3] tellurides[3a,4] as well as ketene telluroacetals,[5] based on Wittig or Wittig-Horner reactions, which represent an important approach to the chalcogenoolefination of carbonyl substrates.

As a further contribution to the study of these classes of compounds, we report herein a further application of the Horner reaction directed at the synthesis of ketene phenyl (or methyl) thio(phenyltelluro)acetals and some characterization of their chemical behavior, such as reactions with *n*-BuLi and capture of the intermediate vinyllithium with electrophiles.

This is of great importance because although some other types of ketene bis(chalcogeno)acetals, such as ketene (thio)-, (seleno)-, (telluro)-, mixed thio(seleno)- and seleno(telluro)acetals have been described in the last years,[6] ketene thio(telluro)acetals continue to be a poorly investigated class of compounds. To our knowledge, the only method reported for their preparation involves the reaction of

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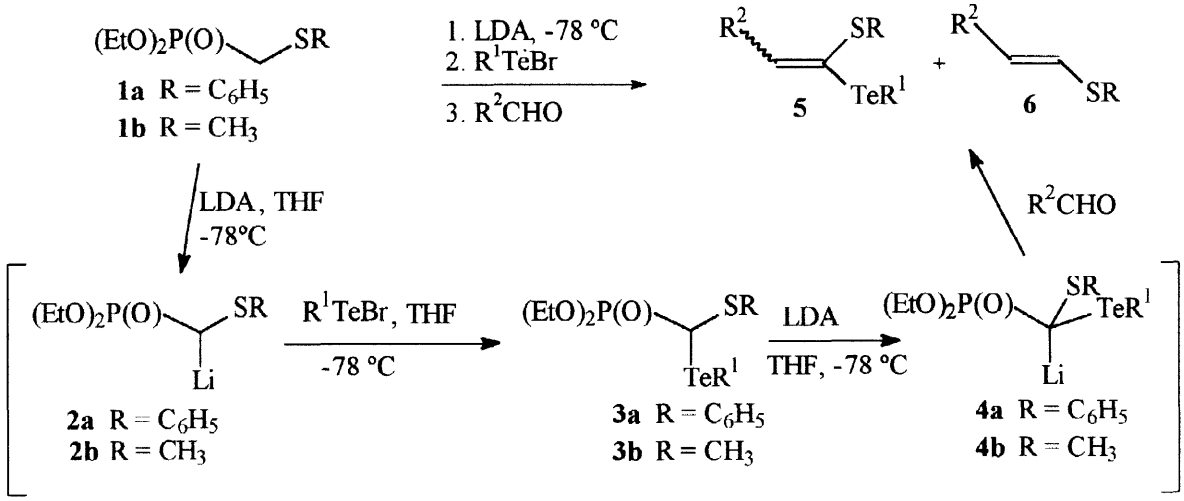
α-methylthio vinyllithium with diphenylditelluride, reported in only two examples,[7] without including Wittig or Horner reactions as a synthetic strategy.

RESULTS AND DISCUSSION

1. Preparation of ketene thio(telluro)acetals

Thiophosphonates **1a** and **1b**, useful intermediate in a variety of important transformations, and easily available on a large scale by the Arbuzov reaction of triethylphosphonate with chloromethyl phenyl (or methyl)sulfide, were selected as starting material.[8] As depicted in Scheme 1, the treatment of **1a,b** with LDA generated the lithiated species **2a,b** which upon reaction with phenyl tellurenyl bromide in THF yielded the thio(telluro)phosphonate intermediates **3a,b**. The deprotonation of **3** at the expense of excess base, followed by the reaction with aldehyde, gives the desired product **5** (Scheme 1) in a one-pot process. As shown in Table 1, good results were obtained with aromatic aldehydes (54-75%), while aliphatic aldehydes provided lower yields and ketones did not react at all with the standard conditions employed.



Scheme 1

It was observed that an excess of thiophosphonate was required to afford good yields of **5**. For example, furfural reacts with equimolar amounts of **1**, providing a 50 % yield of **5b**. However, the yield increases to 55 % and 70 % by using 1.5 and 2 equiv. of the thiophosphonate, respectively. In view of the easy preparation of **1** this excess was used for the present study.

As a consequence of using excess of **1**, in most cases vinylic sulfides **6** were formed together with the desired product **5**. As shown in Table 1 (last column) **6** was isolated in small amount under the mild conditions employed in the present work.[8a,9]

The formation of by-products **6**, which are easily separated by chromatographic purification, can be minimized but not totally avoided even under a variety of experimental conditions. The method exhibits good generality, being successful with several aromatic and aliphatic aldehydes. It is noteworthy that by our method it was possible to prepare the simplest ketene thio(telluro)acetal **5g** derived from formaldehyde, albeit in low yield (38%). Although most of the experiments were performed on a 1.0 mmol scale, the reactions can also be performed successfully on a higher scale, with comparable yields; for example, for **5j** a 68 % yield was observed on a 5-mmol scale.

Concerning the stereochemistry of these olefinations, we usually observed the formation of a mixture of *E* and *Z* products. In the case of aromatic aldehydes, this ratio could not be determined directly since the vinylic hydrogen lies in the aromatic region. Besides, the products were also not stable enough to perform GC analysis, even using different columns and conditions, preventing a direct determination of the *E/Z* ratio. To be sure about the formation of the products as an *E* + *Z* mixture, a ^{125}Te resonance spectroscopy study was performed with some selected examples. The presence of isomers could be easily confirmed since two peaks were observed in the ^{125}Te NMR spectra (157.8 MHz).[10] For example, two peaks at a ratio of 1:1.5 (*E/Z*) at δ 671.1 and 524.5 ppm, and two resonances at δ 667.3 and 529.7 with a ratio of 1:2.5 (*E/Z*) were observed for *p*-chlorobenzaldehyde and benzaldehyde, respectively. The same ratio was observed for the vinylic sulfide obtained by the removal of the tellurium moiety with *n*-BuLi plus ammonium chloride (*vide infra*). These results also confirm the well-known retention of configuration in the tellurium/lithium exchange.[1a,11] In the case of aliphatic aldehydes, the product ratio is directly obtained by analysis of their ^{1}H NMR spectra. In the reaction with butyraldehyde two triplets for the vinylic hydrogens at δ 6.33 and 6.60 with J = 7.2 Hz were observed at a 1:1 ratio. This result was confirmed by tellurium resonance where two peaks of equal intensity appeared at δ 630.1 and 455.7. Likewise, in the reaction with isobutyraldehyde two doublets (1:1.4; *E/Z* ratio, J = 9.2 Hz) were observed at δ 6.15 (for the *Z* isomer, vinylic H) and 6.47 (for the *E* isomer). The experimental results of the synthesis of compounds **5** are summarized in Table 1.

Besides the reaction with phenylthio methyl phosphonate **1a,** some reactions with methyl thio methyl phosphonate **1b** were performed (entries 9 and 10, Table 1) under the same experimental conditions. An interesting feature was the fact that the *E/Z* isomers (~1:1 ratio) were easily separable

by column chromatography and that the corresponding vinylic sulfide by-product was not formed. The more polar isomer was shown to have the *Z*-configuration by NOESY NMR.

In these latter cases no formation of the corresponding vinyl sulfides **6i** and **6j** was detected. This is certainly a result of the lower stabilizing capability of the MeS group compared to the PhS moiety, making the lithium methylthio phosphonate (**1-Li**, R = Me) less reactive.

Table 1: Preparation of ketene thio(telluro)acetals 5.

Entry	Product	R	R^1	R^2	Reaction Time (h)[a]	5, Yield (%)	6, Yield (%)
1	**5a**	C_6H_5	C_6H_5	C_6H_5	0.5	75	19
2	**5b**	C_6H_5	C_6H_5	2-Furyl	0.5	70	15
3	**5c**	C_6H_5	C_6H_5	$4\text{-}MeC_6H_4$	0.5	60	30
4	**5d**	C_6H_5	C_6H_5	$4\text{-}ClC_6H_4$	0.5	62	16
5	**5e**	C_6H_5	C_6H_5	$CH_3CH_2CH_2$	1.5	45	17
6	**5f**	C_6H_5	C_6H_5	$(CH_3)_2CH$	1.5	55	16
7	**5g**	C_6H_5	C_6H_5	H	1.5	38	-
8	**5h**	C_6H_5	$CH_3(CH_2)_2CH_2$	2-Furyl	1.5	54	20
9	**5i**	CH_3	C_6H_5	2-Furyl	1.5	67	-
10	**5j**	CH_3	C_6H_5	C_6H_5	1.5	71	-

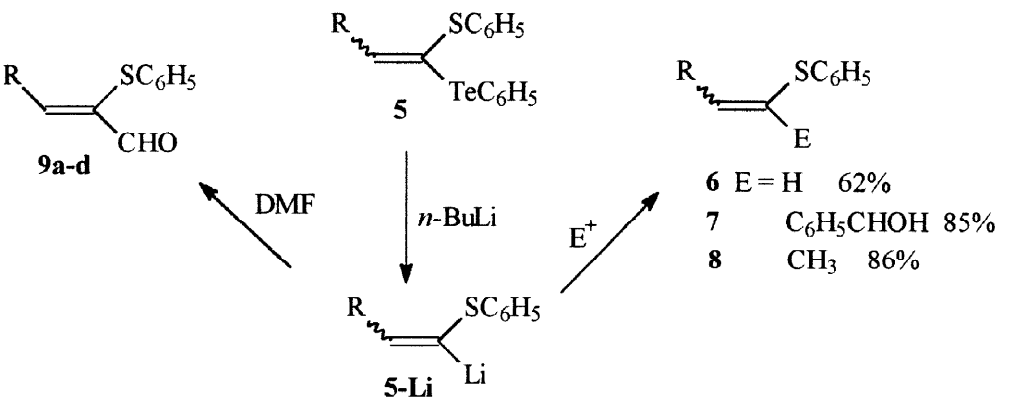
[a] At room temperature.

2. Selective removal of the Tellurium moiety and reaction with electrophiles

As described by many research groups, the tellurium moiety can be easily and selectively removed from vinylic tellurides by treatment with different reagents.[1a,11] A useful method involves treatment with *n*-BuLi leading to the corresponding vinyllithium species,[6b,12,13] which can be submitted to further transformations *in situ*. In the present work we decided to study the selective removal of the Te moiety from ketene thio(telluro)acetals. For this purpose we treated some of the prepared products with *n*-BuLi at –78 °C and reacted the intermediate vinyllithium with electrophiles. In addition,

selective removal of the tellurium moiety by Te/Li exchange reaction and analysis of the vinylic sulfide obtained could give information about the stereochemistry of the ketene thio(telluro)acetals formation. The results are summarized in Scheme 2 and Table 2.

The lithium-tellurium exchange reaction on **5a** (1:2.5; *E/Z* ratio, *vide infra*) with *n*-BuLi, followed by treatment with aqueous ammonium chloride furnished the corresponding vinylic sulfide **6** (Table 2, entry 2) in 62% yield as an *E/Z* mixture at a 2.5:1 ratio as deduced by ^{1}H NMR analysis of their vinylic hydrogens (δ = 6.69 and 6.85, 15.6 Hz for the *E*-isomer and δ = 6.45 and 6.55, 10.8 Hz for the *Z*-isomer). In addition to the vinylic sulfide, BuTePh, BuTeBu and PhTePh were isolated (normal byproducts of reaction of vinylic phenyl tellurides with *n*-BuLi).[14] The **5a-Li** intermediate was also converted to the corresponding allylic alcohol **7** by reaction with benzaldehyde in 85% yield (Table 2, entry 1).[11b] The product was an *E/Z* mixture of isomers (1.7:1 ratio), as determined by ^{1}H NMR. The same reaction with methyl iodide gave the corresponding tri-substituted vinylic sulfide **8** in good isolated yield (86%, *E/Z*, 1.9:1, Table 2, entry 3).

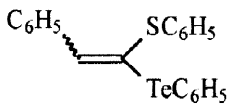
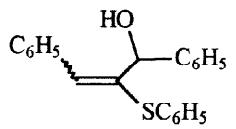
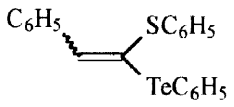
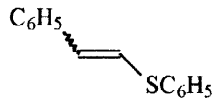
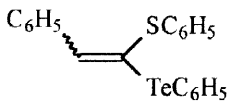
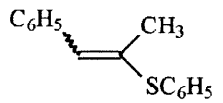
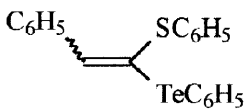
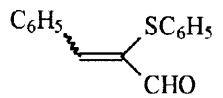
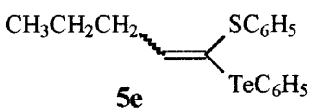
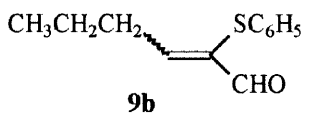
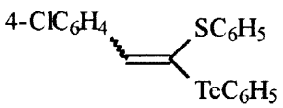
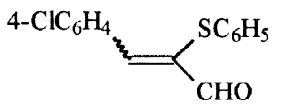
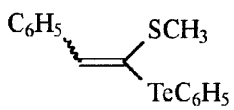
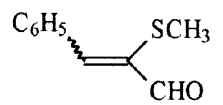


Scheme 2

Of great synthetic interest is the reaction of the intermediate α-lithium vinylic sulfide with DMF, giving the corresponding α-phenylthio-α,β-unsaturated aldehydes **9a-d**. This almost unknown class of compounds has recently been prepared by the reaction of 1-lithio-2-ethoxy vinyl sulfides with aldehydes and ketones followed by acid-catalyzed dehydration.[13] Regardless of the geometry of the ketene thio(telluro)acetal used, the products exhibited almost exclusively the most stable *Z*-configuration, with only trace amounts of the *E*-isomer, as detected by ^{1}H NMR (400 MHz). The *Z*-configuration was confirmed by a NOE experiment. This result was also confirmed by the ^{13}C NMR spectra where single peaks for all carbons were observed. In this way, even starting with an *E+Z* mixture of ketene (S, Te)acetals only the most stable *Z*-isomer is formed under the reaction conditions.

In summary, in this paper we report a general synthesis of ketene (S, Te)acetals and studies on their reactivity by reaction with *n*-BuLi and capture of the intermediate vinyllithium with electrophiles.

Table 2: Products from the Te/Li exchange reaction on ketene phenyltelluro(thio)acetals 5.

Entry	Reagent	E^+	Products	Yield (%)	Ratio[a] (*E*/*Z*)
1	 **5a**	C_6H_5CHO	 **7**	85	1.7:1
2	 **5a**	H_2O	 **6**	62	2.5:1
3	 **5a**	CH_3I	 **8**	86	1.9:1
4	 **5a**	DMF	 **9a**	63	1:16
5	 **5e**	DMF	 **9b**	40	< 1:20
6	 **5d**	DMF	 **9c**	58	1:16
7	 **5j**	DMF	 **9d**	62	< 1:25

[a] Determined by ^1H NMR of the crude reaction mixture and compared after purification.

EXPERIMENTAL SECTION

General Remarks. ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with a 200 MHz, 300 MHz or a 400 MHz spectrometer as noted. Chemical shifts are expressed as parts per million (ppm) downfield from tetramethylsilane as an internal standard. Mass spectra (EI) were obtained at 70 eV with a Hewlett Packard EM/CG HP-5988A spectrometer, infra-red were acquired on a Perkin-Elmer 1310 Spectrometer and elemental analyses were performed on a Vario EL Elementar Analysensysteme. Merck's silica gel (230-400 mesh) was used for flash chromatography. THF was distilled over sodium/benzophenone immediately before use. The thiophosphonates[8] and PhTeBr[15] were prepared by literature methods.

General procedure for the synthesis of ketene (S,Te)-acetals. To a solution of LDA (3.1 mmol) in THF (4 mL) cooled to -78 °C, under nitrogen, was added dropwise a solution of **1** (2 mmol) in THF (1 mL). The reaction was stirred at this temperature for 30 minutes after which PhTeBr (1 mmol) in THF (2 mL) was added. At the beginning the tellurium consumption was fast but by the end of the addition a slightly red solution remained, which became yellow in ca. 20 min. The temperature was raised to 0 °C for 30 minutes, the aldehyde (1 mmol) was then added and the reaction mixture stirred for one hour at 0 °C and for 30-90 min at room temperature (see Table 1). The reaction was treated with water and extracted with ethyl acetate (3 × 25 mL). The organic layer was dried over $MgSO_4$ and the solvent removed under vacuum. The residue was purified by column chromatography and eluted with hexane, yielding **5a-j** (mixture of isomers).

(*E*+*Z*)-2-Phenyl-1-phenylsulfanyl-1-phenyltellanyl-1-ethene (5a)

Yield 0.312g (75%). MS *m/z* (rel. int.) 211 (M^+ -C_6H_5Te, 100.0), 207 (11.5), 178 (63.9), 165 (44.8), 109 (30.1), 77 (46.8); ^1H NMR (300 MHz, $CDCl_3$) δ 7.00-7.45 (m, 11H), 7.58 (s, 1H, vinylic), 7.70-7.90 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 111.4, 112.7, 114.4, 116.2, 127.1, 127.5, 127.6, 127.7, 128.0, 128.1, 128.2, 128.4, 128.6, 128.7, 128.8 (2C), 129.0, 129.4, 131.1, 131.4, 135.8, 135.9, 137.3, 138.6, 139.4, 140.0, 141.0, 144.0. Anal. Calcd. for $C_{20}H_{16}STe$: C, 57.74; H, 3.88. Found: C, 57.56; H, 3.82.

(*E*+*Z*)- 2-(2-Furyl)-1-phenylsulfanyl-1-phenyltellanyl-1-ethene (5b)

Yield 0.284g (70%). MS *m/z* (rel. int.) 408 (M^+, 69.32), 201 (78.2), 173 (100.0), 77 (86.2); ^1H NMR (400 MHz, $CDCl_3$) δ (*Z*) and (*E*) 6.38-6.42 (m, 1.7H), 6.80 (d, J = 3.2 Hz, 0.3H), 7.00 (s, 0.3H), 7.07-7.40 (m, 9H), 7.48-7.49 (m, 0.7H), 7.64-7.67 and 7.72-7.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.4, 109.3, 110.6, 111.0, 111.7, 114.8, 115.9, 126.7, 127.9, 128.1, 128.4, 128.5, 128.6, 128.7, 128.8, 129.5, 130.2, 132.5, 135.3, 136.2, 139.5, 141.2, 141.4, 142.4, 152.4, 152.6. Anal. Calcd. for $C_{18}H_{14}OSTe$: C, 53.25; H, 3.48. Found: C, 53.11; H, 3.43.

(*E*+*Z*)- 2-(4-Methylphenyl)-1-phenylsulfanyl-1-phenyltellanyl-1-ethene (5c)

Yield: 0.258g (60%). MS *m/z* (rel. int.) 225 (M^+ -C_6H_5Te, 100.0), 210 (88.9), 77 (84.9); ^1H NMR (400 MHz, $CDCl_3$) δ 2.31 (*E*) and 2.34 (*Z*) (2s, 3H), 7.07-7.44 (m, 13H), 7.59-7.62 and 7.75-7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.3, 109.7, 111.4, 114.6, 116.3, 126.9, 127.3, 128.1, 128.2, 128.3, 128.6, 128.7(2C), 128.8, 128.9, 129.0, 129.4, 130.8, 131.2, 134.6, 135.8, 136.1, 136.2, 137.6, 137.7, 139.3, 140.1, 141.9, 144.9. Anal. Calcd. for $C_{21}H_{18}STe$: C, 58.65; H, 4.22. Found: C, 58.38; H, 4.17.

(*E*+*Z*)-2-(4-Chlorophenyl)-1-phenylsulfanyl-1-phenyltellanyl-1-ethene (5d)

Yield 0.279g (62%). MS *m/z* (rel. int.) 452 (M^+, 24.3), 245 (56.4), 210 (100.0), 77 (38.2); ^1H NMR (200 MHz, $CDCl_3$) δ 7.07-7.43 (m, 13H), 7.57-7.78 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 112.8, 114.1, 114.3, 116.1, 127.6, 127.8, 128.2, 128.3, 128.6, 128.8, 128.9, 129.0, 129.5, 129.6, 130.1, 130.6, 131.6, 131.7, 133.2, 133.4, 135.5, 135.6, 135.8, 137.1, 138.6, 139.7, 139.8, 141.7. Anal. Calcd. for $C_{20}H_{15}ClSTe$: C, 53.33; H, 3.36. Found: C, 53.46; H, 3.32.

(*E*+*Z*)-1-Phenylsulfanyl-1-phenyltellanyl-1-pentene (5e)

Yield 0.172g (45%). MS *m/z* (rel. int.) 382 (M^+-2, 4.4), 284 (33.7), 207 (19.2), 177 (29.4), 154 (85.0), 77 (100.0); ^1H NMR (200 MHz, $CDCl_3$) δ 0.86-0.95 (m, 3H), 1.33-1.52 (m, 2H), 2.20-2.31 and 2.33-2.44 (m, 2H), 6.33 and 6.60 (2t, J = 7.2 Hz, 1H; vinylic), 7.08-7.31 (m, 8H), 7.57-7.63 and 7.68-7.73 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.7, 13.8, 22.1, 22.2, 34.6, 38.9, 106.4, 110.0, 114.4, 115.6, 126.6, 126.8, 127.9, 128.1, 128.8 (2C), 129.0, 129.2, 130.1, 130.4, 136.5, 136.6, 138.9, 139.0, 147.7, 152.3. Anal. Calcd. for $C_{17}H_{18}STe$: C, 53.45; H, 4.75. Found: C, 53.26; H, 4.66.

(*E*+*Z*)-3-Methyl-1-phenylsulfanyl-1-phenyltellanyl-1-butene (5f)

Yield 0.210g (55%). MS *m/z* (rel. int.) 382 (M^+-2, 3.2), 284 (33.6), 207 (20.0), 177 (16.9), 154 (100.0), 77 (75.7); ^1H NMR (200 MHz, $CDCl_3$) δ 1.00 and 1.01 (2d, J = 6.8 Hz, 3H), 2.61-2.79 and 2.97-3.16 (m, 1H), 6.15 (*Z*) and 6.47 (*E*) (2d, J = 9.2 Hz, 1H; vinylic), 7.09-7.29 (m, 8H) 7.58-7.70 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.1 (2C), 22.3 (2C), 32.0, 36.8, 104.1, 107.0, 114.4, 115.7, 126.6, 126.7, 127.9, 128.0, 128.8(2C), 128.9, 129.2, 130.0, 130.3, 136.5, 136.6, 138.6, 138.9, 154.7, 159.7. Anal. Calcd. for $C_{17}H_{18}STe$: C, 53.45; H, 4.75. Found: C, 53.10; H, 4.65.

(*E*+*Z*)-1-Phenylsulfanyl-1-phenyltellanylethylene (5g)

Yield 0.129g (38%). MS *m/z* (rel. int.) 342 (M^+, 12.7), 207 (4.2), 135 (100.0), 91 (48.8), 77 (15.6); ^1H NMR (200 MHz, $CDCl_3$) δ 5.79 (s, 1H), 6.11 (s, 1H), 7.21-7.46 (m, 8H), 7.78-7.83 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 114.7, 117.5, 126.7, 128.4, 129.2, 129.4, 133.1, 134.6, 139.0. Anal. Calcd. for $C_{14}H_{12}STe$: C, 49.47; H, 3.56. Found: C, 49.49; H, 3.48.

(*E*+*Z*)-1-Butyltellanyl-2-(2-furyl)-1-phenylsulfanyl-1-ethene (5h)

Yield 0.208g (54%). MS *m/z* (rel. int.) 388 (M^+, 10.3), 201 (39.8), 183 (24.5), 173 (100.0); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.80-0.91 (m, 3H), 1.21-1.42 (m, 2H), 1.56-1.81 (m, 2H), 2.76-2.87 (m, 2H), 6.40-6.43 (m, 1H), 6.48-6.50 and 6.88-6.89 (2m, 1H), 7.10-7.46 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.0, 11.1, 13.3 (2C), 25.1, 25.2, 33.4, 33.9, 103.8, 104.4, 110.8, 111.1, 111.5, 111.7, 126.8, 127.5, 128.8, 129.1, 129.5, 130.3, 131.5, 132.1, 136.1, 136.9, 141.4, 142.1, 152.5, 152.6. Anal. Calcd. for $C_{16}H_{18}OSTe$: C, 49.79; H, 4.70. Found: C, 50.24; H, 4.52.

(*E*)-2-(2-Furyl)-1-methylsulfanyl-1-phenyltellanyl-1-ethene (5i)

Yield 0.120g (35%). MS *m/z* (rel. int.) 346 (M^+, 22.3), 207 (5.7), 139 (100.0), 124 (74.4), 77 (63.3); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.34 (s, 3H), 6.42-6.45 (m, 1H), 6.80-6.82 (m, 1H), 7.15-7.40 (m, 4H), 7.34 (s, 1H), 7.70-7.75 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.5, 111.6, 111.7, 112.1, 115.8, 127.9, 129.6, 131.9, 137.0, 141.4, 152.7. Anal. Calcd. for $C_{13}H_{12}OSTe$: C, 45.40; H, 3.52. Found: C, 45.21; H, 3.46.

(*Z*)-2-(2-Furyl)-1-methylsulfanyl-1-phenyltellanyl-1-ethene (5i)

Yield 0.110g (32%). MS *m/z* (rel. int.) 346 (M^+, 8.7), 205 (4.2), 139 (64.7), 55 (100.0); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.26 (s, 3H), 6.35-6.41 (m, 2H), 6.75 (s, 1H), 7.20-7.42 (m, 4H), 7.88-7.93 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.4, 108.2, 110.9, 111.3, 113.7, 117.8, 128.7, 129.0, 140.6, 141.3, 153.1. Anal. Calcd. for $C_{13}H_{12}OSTe$: C, 45.40; H, 3.52. Found: C, 44.96; H, 3.31.

(*E*)-1-Methylsulfanyl-2-phenyl-1-phenyltellanyl-1-ethene (5j)

Yield 0.142g (40%). MS *m/z* (rel. int.) 356 (M^+, 4.9), 207 (5.0), 149 (79.9), 134 (100.0); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.29 (s, 3H), 7.14-7.38 (m, 6H), 7.45 (s, 1H), 7.51-7.57 (m, 2H), 7.75-7.80 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.3, 115.5, 116.0, 127.4, 127.9, 128.0, 129.2, 129.5, 137.3, 137.7, 144.6. Anal. Calcd. for $C_{15}H_{14}STe$: C, 50.90; H, 3.99. Found: C, 51.02; H, 4.17.

(*Z*)-1-Methylsulfanyl-2-phenyl-1-phenyltellanyl-1-ethene (5j)

Yield 0.110g (31%). MS *m/z* (rel. int.) 356 (M^+, 5.9), 207 (4.5), 149 (82.0), 134 (100.0); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.30 (s, 3H), 6.86 (s, 1H), 7.13-7.32 (m, 8H), 7.73-7.79 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.5, 113.8, 113.9, 127.0, 128.0, 128.1, 128.2, 129.0, 131.2, 139.1, 139.2. Anal. Calcd. for $C_{15}H_{14}STe$: C, 50.90; H, 3.99. Found: C, 50.87; H, 4.24.

(*Z,E*)-1,3-Diphenyl-2-phenylsulfanyl-2-propen-1-ol 7 from 5a. To a solution of **5a** (0.416g, 1 mmol) in THF (4 mL) at -78 °C under nitrogen was added dropwise a solution of *n*-BuLi (0.50 mL, 1.1 mmol, 2.22 M solution

in hexane). After 20 minutes of stirring at this temperature, benzaldehyde (0.159g, 1.5 mmol) was added. The mixture was stirred for 1 h at –78 °C, then diluted with ethyl acetate (30 mL) and washed with brine (4 × 15 mL). The organic layer was separated and dried over $MgSO_4$ and the solvent was removed under vacuum. The residue was purified by column chromatography over silica gel. Elution with hexane removed dibutyl, diphenyl and butyl phenyl tellurides, and elution with ethyl acetate yielded 7 as an oil. Yield 0.270g (85%). MS *m/z* (rel. int.) 318 (M^+, 51.9), 211 (71.1), 178 (64.8), 77 (100.0); ^1H NMR (300 MHz, $CDCl_3$) δ (*Z*) 2.90 (br s, 1H), 5.20 (s, 1H); (*E*) 3.00 (d, J = 8 Hz, 1H), 6.00 (d, J = 8.00 Hz, 1H); (*E*) and (*Z*) 6.66 (s, 0.7H; vinylic), 7.00-7.70(m, 15.3H); ^{13}C NMR (50 MHz, $CDCl_3$) (*E* + *Z*) δ 71.1, 76.6, 126.0, 126.2, 126.8, 127.4, 127.5, 127.8, 127.9, 128.2, 128.4, 128.9, 129.1, 129.2, 129.4, 132.3, 133.4, 134.2, 134.3, 134.4, 135.4, 135.5, 135.9, 141.1, 141.4, 141.5. Anal. Calcd. for $C_{21}H_{18}OS$: C, 79.21; H, 5.70. Found: C, 78.24; H, 5.85.

(*Z,E*)-1-Phenyl-2-phenylsulfanyl-1-propene (8)

Yield 0.194g (86%). MS *m/z* (rel. int.) 226 (M^+, 98.3), 167 (42.6), 115 (100.0), 91 (28.9); ^1H NMR (200 MHz, $CDCl_3$) δ 2.03 (*Z*) and 2.13 (*E*) (2d, J = 1.4Hz, 3H); 6.70 (s, 1H; vinylic, minor isomer), 7.20-7.57 (m, 11H; includes 1H vinylic, major); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.6, 25.6, 126.0, 126.7, 127.0, 127.2, 127.4, 128.0, 128.2, 128.3, 128.7, 128.8, 128.9, 129.0, 129.1, 130.1, 130.8, 130.9, 131.7, 132.1, 133.7, 136.9. Anal. Calcd. for $C_{15}H_{14}S$: C, 79.60; H, 6.23. Found: C, 79.56; H, 6.04.

(*Z,E*)-1-Phenyl-2-phenylsulfanyl-1-ethene (6)[3]

Yield 0.131g (62%). ^1H NMR (200 MHz, $CDCl_3$) δ (*Z*) 6.45 (d, J = 10.8 Hz, 0.3H), 6.55 (d, J = 10.8 Hz, 0.3H); (*E*) 6.69 (d, J = 15.6 Hz, 0.7H), 6.85 (d, J = 15.6 Hz, 0.7H); (*E* + *Z*) 7.13-7.55 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 123.3, 125.9, 126.00, 126.8, 127.0, 127.1, 127.2, 127.5, 128.2, 128.6, 128.7, 129.1, 129.7, 129.9, 131.7, 135.2, 136.2, 136.3, 136.4, 137.9.

Synthesis of (*Z*)-3-Phenyl-2-phenylsulfanyl-2-propenal 9a from 5a. To a solution of **5a** (0.416g, 1.0 mmol) in THF (4 mL) at -78 °C under nitrogen was added dropwise a solution of *n*-BuLi (0.50 mL, 1.1 mmol, 2.22 M solution in hexane). After 20 minutes of stirring at this temperature, DMF (0.1 mL, 1.29 mmol) was added. The temperature was raised to room temperature and stirred for 2 hours, then diluted with ethyl acetate (30 mL), and washed with water (3 × 20 mL). The organic layer was separated and dried with $MgSO_4$ and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel. Elution with hexane removed dibutyl, diphenyl and butyl phenyl tellurides, and ethyl acetate was used to elute the pure compound **9a**. Yield: 0.151g (63%). MS *m/z* (rel. int.) 240 (M^+, 100.0), 211 (46.3), 178 (44.9), 131 (35.7), 110 (16.0); IR (KBr, cm^{-1}): 1669 (CO). ^1H NMR (400 MHz, $CDCl_3$) δ 7.15-7.29 (m, 5H), 7.43-7.45 (m, 3H), 7.88 (s, 1H), 7.95-8.00 (m, 2H), 9.55 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 126.5, 128.5, 128.9, 129.0, 131.0, 131.2, 133.0, 133.5, 133.6, 150.9, 190.6. Anal. Calcd. for $C_{15}H_{12}OS$: C, 74.97; H, 5.03. Found: C, 74.73; H, 5.18.

(*Z*)-2-Phenylsulfanyl-2-hexenal (9b)

Yield: 0.082g (40%). MS *m/z* (rel. int.) 206 (M^+, 100.0), 177 (21.0), 135 (62.6), 110 (55.5); IR (film, cm^{-1}): 1690 (CO). ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J = 7.4 Hz, 3H), 1.56 (sext, J = 7.4 Hz, 2H), 2.58-2.64 (m, 2H), 7.12-7.25 (m, 5H), 7.25 (t, J = 7.4Hz, 1H), 9.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.5, 32.7, 126.2, 128.6, 128.9, 134.3, 136.6, 161.0, 190.1. Anal. Calcd. for $C_{12}H_{14}OS$: C, 69.86; H, 6.84. Found: C, 69.15; H, 6.89.

(*Z*)-3-(4-Chlorophenyl)-2-phenylsulfanyl-2-propenal (9c)

Yield 0.159g (58%). MS *m/z* (rel. int.) 274 (M^+, 43.9), 239 (47.3), 210 (100.0), 165 (62.7), 110 (64.7); IR (film, cm^{-1}): 1690 (CO). ^1H NMR (200 MHz, $CDCl_3$) δ 7.14-7.28 (m, 5H), 7.35-7.42 (m, 2H), 7.80 (s, 1H), 7.86-7.93 (m, 2H), 9.51 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 126.9, 128.9, 129.1, 129.2, 132.0, 132.4, 133.2, 133.5, 137.0, 148.8, 190.5. Anal. Calcd. for $C_{15}H_{11}OSCl$: C, 65.57; H, 4.04. Found: C, 65.42; H, 4.25.

(*Z*)-2-Methylsulfanyl-3-phenyl-2-propenal (9d)

Yield 0.110g (62%). MS *m/z* (rel. int.) 178 (M^+, 51.7), 134 (100.0), 102 (46.5), 91 (53.3); IR (film, cm^{-1}): 1685 (CO). ^1H NMR (200 MHz, $CDCl_3$) δ 2.39 (s, 3H), 7.26-7.50 (m, 3H), 7.52 (s, 1H), 7.85-7.90 (m, 2H), 9.54 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.9, 128.4, 130.4, 131.0, 134.0, 137.3, 150.6, 191.2. Anal. Calcd. for $C_{10}H_{10}OS$: C, 67.38; H, 5.65. Found: C, 67.29; H, 5.66.

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REFERENCES

1. (a) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373. (b) Comasseto, J. V. *J. Organomet. Chem.* **1983**, *253*, 131. (c) Petragnani, N. "*Best Synthetic Methods - Tellurium in Organic Synthesis*", Academic Press, **1994**.

2. (a) Katritzky, A. R.; Meth-Cohn, O.; Rees, C. W. "*Comprehensive Organic Functional Group Transformations*", Pergamon, London, **1995**. (b) Nebois, P.; Kann, N.; Greene, A. E. *J. Org. Chem.* **1995**, *60*, 7690 and references therein.

3. (a) Silveira, C. C.; Begnini, M. L.; Boeck, P.; Braga, A. L. *Synthesis* **1997**, 221. (b) Silveira, C. C.; Perin, G.; Braga, A. L. *J. Chem. Res (S)* **1994**, 492.

4. **Silveira, C. C.; Perin. G.; Braga, A. L.; Petragnani, N.** *Synlett* **1995**, 58.

5. **Silveira, C. C.; Perin, G.; Braga, A. L.** *Tetrahedron Lett.* **1995**, *36*, 7361.

6. For a review on ketene thioacetals, see: **Kolb, M.** *Synthesis* **1990**, 171. (a) Brobel. B. T.; Seebach. D. *Chem Ber.* **1977**, *110*, 852. (b) Harirchian, B.; Magnus, P. *Chem. Commun.* **1977**, 522. (c) Denis, J. N.; Desauvage, S.; Hevesi, L.; Krief, A. *Tetrahedron Lett.* **1981**, *22*, 4009. (d) Denis, J. N.; Krief, A. *Tetrahedron Lett.* **1982**, *23*, 3407. (e) Cristau, H. J.; Chabaud, B.; Labaudiniere, R.; Christol, H. *J. Org. Chem.* **1986**, *51*, 875. (f) Shin, W. S.; Lee, K. S.; Oh, D. Y. *Tetrahedron Lett.* **1992**, *33*, 5375. (g) Degl'Innocenti, A.; Ulivi, P.; Capperucci, A.; Mordini, A.; Reginato, G.; Ricci, A. *Synlett* **1992**, 499. (h) Braga, A. L.; Reckziegel, A.; Silveira, C. C.; Comasseto, J. V. *Synth. Commun.* **1994**, *24*, 1165. (i) Dabdoub, M. J.; Cassol, T. M.; Barbosa, S. L. *Tetrahedron Lett.* **1996**, *37*, 831. (j) Stefani, H. A.; Comasseto, J. V.; Petragnani, N.; Braga, A. L.; Menezes, P. H.; Gusevskaya, E. V. *Phosphorus, Sulfur and Silicon* **1997**, *126*, 211. (k) Dabdoub, M. J.; Begnini, M. L.; Guerrero Jr., P. G. *Tetrahedron* **1998**, *54*, 2371.

7. Braga, A. L.; Zeni, G.; Andrade, L. H.; Silveira, C. C. *Synlett* **1997**, 595.

8. (a) Shahak, I.; Almog, J. *Synthesis* **1969**, 170; (b) Green, M. *J. Chem Soc.* **1963**, 1324.

9. Corey, E. J.; Shulman, J. I. *J. Org. Chem.* **1970**, *35*, 777. Mikolajczyk, M.; Grzejszczak, S.; Midura, W.; Zatorski, A. *Synthesis* **1975**, 278.

10. Stefani, H. A.; Campos, I. P. A.; Roque, L. C.; Montoro, M. A.; Braga, A. L. *J. Chem. Res.(S)* **1996**, 54.

11. (a) Hiiro, T.; Kambe, N.; Ogawa, A.; Miyoshi, N.; Murai, S.; Sonoda, N. *Angew. Chem. Intl. Ed. Engl.* **1987**, *26*, 1187. (b) Barros, S. M.; Dabdoub, M. J.; Dabdoub, V. B.; Comasseto, J. V. *Organometallics* **1989**, *8*, 1661. (c) Dabdoub, M. J.; Dabdoub, V. B. *Tetrahedron* **1995**, *47*, 9839. (d) Dabdoub, M. J.; Cassol, T. M. *Tetrahedron* **1995**, *47*, 12971. (e) Tucci, F. C.; Chieffi, A.; Comasseto, J. V.; Marino, J. P. *J. Org. Chem.* **1996**, *61*, 4975.

12. Oshima, K.; Shimoji, K.; Takahashi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1973**, *95*, 2694. Muthukrishnan, R.; Schlosser, M. *Helv. Chim. Acta* **1976**, *59*, 13. Vlattas, I.; Dalla Vecchia, L.; Lee, A. O. *J. Am. Chem. Soc.* **1976**, *98*, 2008. Cookson, R. C.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1976**, 990. Everhardus, R. H.; Eeuwhorst, H. G.; Brandsma, L. *J. Chem. Soc., Chem. Commun.* **1977**, 801. Schmidt, R. R.; Schmid, B. *Tetrahedron Lett.* **1977**, 3583. Everhardus, R. H.; Grafing, R.; Brandsma, L. *Rec. Trav. Chim Pays-Bas* **1978**, *97*, 69. Braun, M. *Tetrahedron Lett.* **1978**, 3695. Fitt, J. J.; Gschwend, H. W. *J. Org. Chem.* **1979**, *44*, 303. Cohen, T.; Weisenfeld, R. B. *J. Org. Chem.* **1979**, *44*, 3601. Cohen, T.; Matz, J. R. *Synth. Commun.* **1980**, *10*, 311.

13. Yoshimatsu, M.; Oguri, K.; Ikeda, K.; Gotoh, S. *J. Org. Chem.* **1998**, *63*, 4475.

14. Barros, S. M.; Comasseto, J. V.; Berriel, J. *Tetrahedron Lett.* **1989**, *30*, 7353.

15. Petragnani, N.; Torres, L.; Wynne, K. J. *J. Organomet. Chem.* **1975**, *92*, 185.