HETEROCYCLES, Vol. 94, No. 10, 2017, pp. 1931 - 1939. © 2017 The Japan Institute of Heterocyclic Chemistry
Received, 26th June, 2017, Accepted, 19th July, 2017, Published online, 1st August, 2017
DOI: 10.3987/COM-17-13773

A CONVENIENT SYNTHESIS OF ISOTELLURAZOLES *VIA* DEOXYGENATION OF ISOTELLURAZOLE *Te*-OXIDE OLIGOMERS BY USING A COMBINATION OF Ph_3P/I_2

Yusuke Taneichi, Kazuaki Shimada,* and Toshinobu Korenaga

Department of Chemistry and Biosciences, Faculty of Science and Engineering, Iwate University, Morioka, Iwate 020-8551, Japan; E-mail: shimada@iwate-u.ac.jp

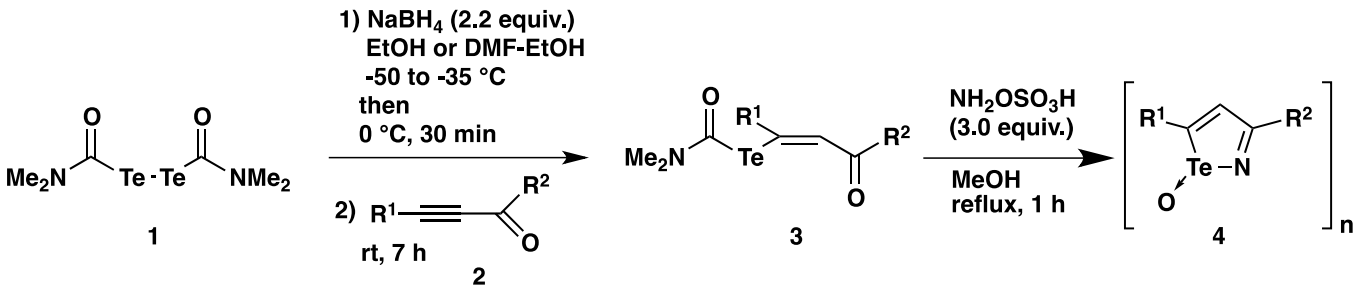
Abstract – Ynones and ynals bearing a variety of substituent were converted into isotellurazole *Te*-oxide oligomers through a convenient procedure *via* formation and ring closure of β-(*N,N*-dimethylcarbamoyltellurenyl)alkenyl ketones or aldehydes, and the subsequent conversion of **A** into the corresponding isotellurazoles **B** was carried out efficiently by treating with Ph_3P/I_2 under a rather mild reaction condition.

Recently, hetero Diels-Alder reactions have been widely recognized as one of the most effective methods for the syntheses of various heterocycles, and especially, the thermal reactions of higher-row chalcogenazoles and isochalcogenaozles have been of great interest in line with the synthetic potentiality of these compounds,[1,2] and especially isotellurazoles having a tellurium-bridged cisoid heterodiene along with a weak carbon-tellurium and nitrogen-tellurium bonds and the enhanced ring strain of the ring systems involving a tellurium atom with a large atomic radius. However, the synthetic methods of isotellurazoles have been strictly limited because of the difficulty in the preparation of suitable precursors. In the course of our synthetic research work on the synthesis of higher-row chalcogen-containing heteroaromatic compounds, we have previously reported a preparation of isoselenazoles and isotellurazoles through a four-step procedure starting from ynones and bis(*N,N*-dimethylcarbamoyl) diselenide or ditelluride, respectively.[3] Especially, isotellurazole *Te*-oxides were formed in all cases by treating β-(*N,N*-dimethylcarbamoyltelluro)alkenyl ketones with NH_2OSO_3H, and deoxygenation of those products required the treatment with Ph_3P at rather high reaction temperature. In addition, treatment of isotellurazole *Te*-oxides with a variety of acetylenic dienophiles for hetero Diels-Alder reaction just gave substituted pyridines in much lower yields as the cycloadducts in all cases along with the formation of several byproducts in contrast to the cases using isotellurazoles as heterodienes.[4] Recently, Vargas-Baca

reported the unique tetrameric and/or hexameric macrocyclic structures of **4** for isotellurazole *Te*-oxides (isotellurazole *N*-oxides) obtained through the similar procedure,[5] and this result suggested the disfavor in the synthetic use of isotellurazole *Te*-oxide oligomers **4** as the heterodienes for hetero Diels-Alder reaction in contrast to isotellurazoles. Through the requirement for the use of isotellurazoles **5** as reactive heterodienes for the synthesis of azafluorenone alkaloid skeletons, we attempted the modification of our previous procedure involving the deoxygenation of isotellurazole *Te*-oxide oligomers **4** by applying the combination of Ph_3P with an electrophilic activator in line with the previous reports on deoxygenation of epoxides and sulfoxides.[6] Finally, we found a novel and efficient procedure for deoxygenation of isotellurazole *Te*-oxide oligomers **4** by treating with Ph_3P and I_2, and in this paper we would like to report the details of the efficient and convenient preparation of mono- and disubstituted isotellurazoles **5** involving the synthetic scope and limitation.

Isotellurazole *Te*-oxide oligomers **4** were at first prepared through a three-step procedure starting from bis(*N*,*N*-dimethylcarbamoyl) ditelluride (**1**) [(1) $NaBH_4$ (2.2 equiv.), (2) ynone or ynal **2** bearing a variety of substituents at R^1 and an alkyl group or hydrogen atom for R^2, (3) NH_2OSO_3H (3.0 equiv.)], and compounds **4** were subsequently subjected to deoxygenation by treating with Ph_3P at high temperature in a sealed tube in order for the preparation of authentic isotellurazoles **5**.[3] Our previous attempts for deoxygenation of isotellurzole *Te*-oxide oligomers **4** by using $NaBH_4$ reduction, Luche reduction, or the treatment of $NH_2NH_2{\bullet}H_2O$ were not successful at all except for the treatment with Ph_3P under the condition of high temperature in a sealed tube. Furthermore, isotellurazole *Te*-oxide oligomer **4b** bearing two alkyl substituents at the R^1 and R^2 positions was unexpectedly inactive toward Ph_3P reduction under the similar condition even after the prolonged reaction time, and this phenomenon just limited the synthetic use of isotellurazoles.

Table 1. Preparation of Isotellurazole *Te*-Oxide Oligomers **4**



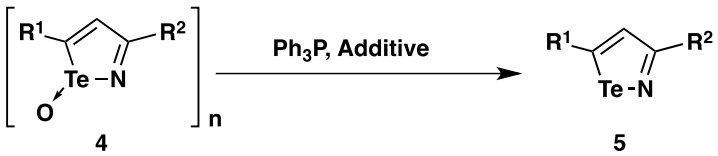
Ynone **2**		Yield (%)	
R^1	R^2	**3**	**4**
C_6H_5	Me	94 (**3a**)	81 (**4a**)[a]
n-C_4H_9	Me	75 (**3b**)	74 (**4b**)
t-C_4H_9	Me	92 (**3c**)	98 (**4c**)

n-C_4H_9	H	91 (**3d**)	46 (**4d**)
C_6H_5	H	69 (**3e**)	75 (**4e**)
Me	H	93 (**3f**)	64 (**4f**)

[a]See reference 3.

When a toluene solution of isotellurazole *Te*-oxide oligomer **4a** was treated with Ph_3P (2.2 equiv.) at refluxing temperature for 168 h, the corresponding isotellurazole **5a** was obtained as a sole product in moderate yield. However, the same reaction performed under 0 °C to room temperature only afforded the recovery of substrate **4a**. On the other hand, the reaction condition was dramatically improved by adding I_2 (1.2 equiv.) to the reaction mixture, and the starting compound **4a** underwent facile deoxygenation to afford isotellurazoles **5a** in medium yield even at 0 °C within one or two hours. After the attempts of optimization of the reaction condition, the yield of **5a** was finally raised up to 82% by treating Ph_3P (2.0 equiv.) and I_2 (1.0 equiv.), and the method was applicable to deoxygenation of other isotellurazole *Te*-oxide oligomers **4b**-**f** bearing a variety of R^1 and R^2 substituents involving aryl group, alkyl groups, and hydrogen. It is noteworthy that the combination of Ph_3P-CBr_4 and Ph_3P-$TiCl_4$ was also effective for deoxygenation of **4**. However, in the cases applying the combination of Ph_3P-BF_3•OEt_2, substrate **4a** was quantitatively recovered after the usual quenching procedure using an aqueous $NaHCO_3$ solution. All the results of deoxygenation of isotellurazole *Te*-oxide oligomers **4** by the combination of Ph_3P and an electrophilic activator are summarized in Table 2.

Table 2. Synthesis of Isotellurazoles **5** by Treating Isotellurazole *Te*-Oxide Oligomers **4** with Ph_3P and an Additive



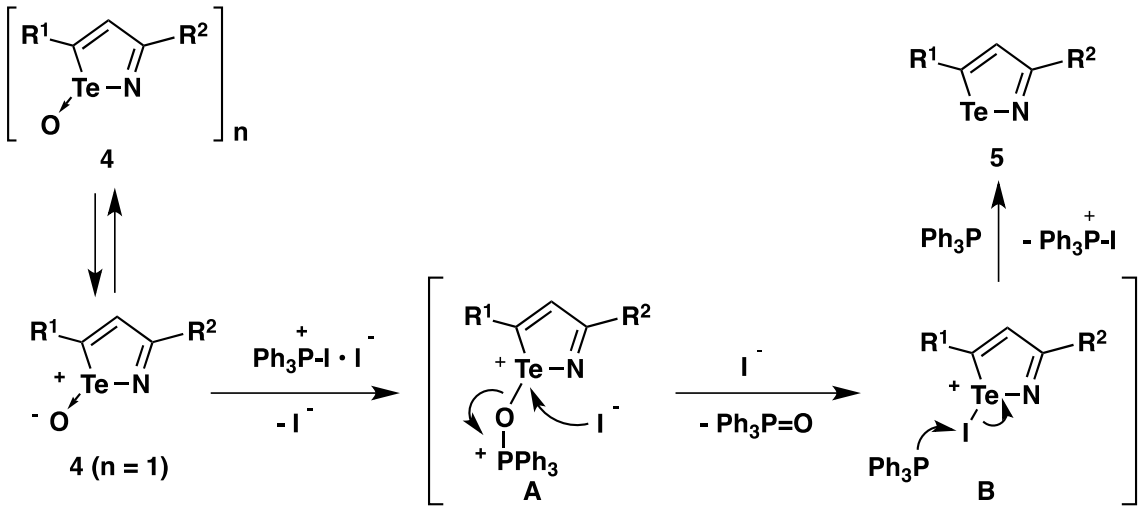
4 5

Substrate / **4**			Ph_3P	Additive	Solvent	Condition		Yield of **5**
R^1	R^2	**4**	(equiv.)	(equiv.)		Temp (°C)	Time (h)	(%)
C_6H_5	Me	**4a**	1.1	-	$CHCl_3$	100	1	91 (**5a**)[a]
C_6H_5	Me	**4a**	2.2	-	toluene	reflux	168	59 (**5a**)
C_6H_5	Me	**4a**	2.0	-	CCl_4	reflux	2	33 (**5a**)
C_6H_5	Me	**4a**	1.2	CBr_4 (1.2)	CH_2Cl_2	0	1	48 (**5a**)
C_6H_5	Me	**4a**	2.0	CBr_4 (1.0)	CH_2Cl_2	0	2	16 (**5a**)
C_6H_5	Me	**4a**	1.2	I_2 (1.2)	CH_2Cl_2	0	2	50 (**5a**)
C_6H_5	Me	**4a**	2.0	I_2 (1.0)	CH_2Cl_2	0	2	82 (**5a**)
C_6H_5	Me	**4a**	2.0	BF_3•OEt_2 (1.0)	CH_2Cl_2	0	2	0[b]

C_6H_5	Me	**4a**	2.0	$TiCl_4$ (1.0)	CH_2Cl_2	0	1	51 (**5a**)
n-C_4H_9	Me	**4b**	2.2	-	toluene	reflux	48	0[c]
n-C_4H_9	Me	**4b**	1.2	CBr_4 (1.2)	CH_2Cl_2	0	1	43 (**5b**)
n-C_4H_9	Me	**4b**	2.0	I_2 (1.0)	CH_2Cl_2	0	3	91 (**5b**)
t-C_4H_9	Me	**4c**	2.0	I_2 (1.0)	CH_2Cl_2	rt	12	73 (**5c**)
n-C_4H_9	H	**4d**	2.0	I_2 (1.0)	CH_2Cl_2	-50	0.5	66 (**5d**)
C_6H_5	H	**4e**	2.0	I_2 (1.0)	CH_2Cl_2	0	2	69 (**5e**)
Me	H	**4f**	2.0	I_2 (1.0)	$CHCl_3$	0	1	80 (**5f**)

[a]Carried out in a sealed tube. See reference 3c. [b]Substrate **4a** was quantitatively recovered after the usual workup procedure. [c]Starting isotellurazole oxide oligomer **4b** was recovered.

Vargas-Baca recently reported that isotellurazole *Te*-oxide oligomers **4** undergo equilibration among a few oligomers in the solution, and therefore the monomeric forms of **4** are assumed to behave as the key intermediates for deoxygenation. The plausible reaction pathway of the deoxygenation of isotellurazole *Te*-oxide oligomers **4** could then be summarized as shown in Scheme 1 involving three step reactions: the primary reaction of Ph_3P-I_2 complex with **4** forming intermediates **A**, subsequent nucleophilic attack of iodide ion to the tellurium atom of **A**, and the final attack of Ph_3P to the iodine atom of intermediates **B** forming isotellurazoles **5** in an analogous manner to that of deoxygenation of sulfoxides.[6] This pathway requires two molar amounts of Ph_3P and one molar amount of I_2 for deoxygenation of **4**, which would be consistent with the experimentally optimized ratio of these reagents.



Scheme 1. Plausible Pathway for Deoxygenation of Isotellurazole *Te*-Oxide Oligomers **4**

It is assumed that the deoxygenation step would be accelerated by the facile fragmentation of isotellurazole *Te*-oxide oligomers **4** through the reaction with iodophosphonium ion (Ph_3P^+-I) with the oxygen atom of monomeric isotellurazole *Te*-oxides **4** (n = 1) in the reaction mixture as well as the facile

elimination of $Ph_3P=O$ from the *in situ* generated intermediates **A** to form intermediates **B** through the strong $Te^{+}\bullet\bullet\bullet I^{-}$ interaction between the tellurium atom of **A** and iodide ion. However, all attempts to carry out the direct observation of plausible intermediates **A** or **B** through a ^1H NMR monitoring of the deoxygenation of **4** using Ph_3P-I_2 in a NMR tube was unsuccessful.

In conclusion, we could find a new procedure for deoxygenation of isotellurzole *Te*-oxide oligomers **4** by using the combination of Ph_3P and I_2. We have already reported that isotellurazoles undergo hetero Diels-Alder reaction to afford substituted pyridines under rather mild conditions, and further synthetic application of alkyl-substituted isotellurazoles for the construction of polycyclic alkaloid skeletons are under way in our laboratory.

EXPERIMENTAL

The melting points were determined with a Barnstead International MEL-TEMP. ^1H NMR spectra were recorded on a Bruker DRX-400P (400 MHz) or Bruker AVANCE III 500 (500 MHz) spectrometer, and the chemical shifts of the ^1H NMR spectra are given in δ relative to internal tetramethylsilane (TMS). ^{13}C NMR spectra were recorded on Bruker DRX-400P (101 MHZ) AVANCE III 500 (126 MHZ). ^{125}Te NMR Spectra were recorded on Bruker AVANCE III 500 (158 MHZ), and the chemical shifts of the ^{125}Te NMR are given in δ relative to Ph_2Te_2 (δ = 421 ppm). Mass spectra were recorded on a JEOL JMS-700T mass spectrometer with electron-impact ionization or electrospray ionization. High resolution mass spectra (HRMS) were also recorded on a JEOL JMS-700T spectrometer. IR spectra were recorded for thin film (neat) or KBr disks on a JASCO FT/IR-7300 spectrometer. Elemental analyses were performed using a Yanagimoto CHN corder MT-5.

Starting Materials. Bis(*N,N*-dimethylcarbamoyl) ditelluride (**1**) was prepared from elemental tellurium, sodium metal or sodium hydride, and *N,N*-dimethylformamide (DMF) according to our previous previous paper.[3a,7] Ynones and ynals (**2**) were prepared through Friedel-Crafts type acylation of terminal acetylenic compounds or oxidation of substituted propargyl alcohols according to the previous papers.[7] All other chemicals used in this study were commercially available.

A Typical Procedure for Preparation of Isotellurazole *Te*-Oxide Oligomers 4 from Bis(*N,N*-dimethylcarbamoyl) Ditelluride (1) and Ynones 2. To DMF or EtOH solution of bis(*N,N*-dimethylcarbamoyl) ditelluride (**1**, 398 mg, 1.00 mmol) was added EtOH solution (5 mL) of $NaBH_4$ (84 mg, 2.2 mol amt.) at -50 °C, and the reaction mixture was then treated with ynone **2** (2.2 mol amt.) at -50 °C to rt for 7 h. The reaction was quenched with aqueous NH_4Cl solution, and the reaction mixture was extracted with CH_2Cl_2. The organic layer was washed twice with water and was dried over anhydrous Na_2SO_4 powder. The organic solvent was removed *in vacuo*, and the residual crude products were subjected to column chromatography on silica gel to obtain *Te*-alkenyl

N,N-dimethyltellurocarbamates **3** in high to moderate yields as yellow oil. Then, MeOH solution (10 mL) of compounds **3** was treated with hydroxylamine-*O*-sulfonic acid (3.0 mol amt.) at reflux for 1 h. The reaction mixture was cooled to room temperature and was quenched with saturated aqueous $NaHCO_3$ solution, and the reaction mixture was subjected to suction filtration to obtain isotellurazole *Te*-oxide oligomers **4** as main products besides a small amount of isotellurazoles **5**.[3c]

4a (R^1 = C_6H_5, R^2 = Me): Pale yellow powder, mp 210.5-211.4 °C (decomp.) (Lit.,[3c] 210.3-211.8 °C (decomp.)).

4b (R^1 = *n*-C_4H_9, R^2 = Me): Yellow needles, mp 131.8-132.5 °C; IR (KBr) 2954, 2927, 2900, 2868, 2855, 1575, 1475, 1464, 1426, 1374, 1232, 1139, 1092, 887, 829, 718, 579 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.5 Hz), 1.36 (2H, sext, *J* = 7.5 Hz), 1.62 (2H, quint, *J* = 7.5 Hz), 2.10 (3H, s), 2.80 (2H, t, *J* = 7.5 Hz), 7.09 (1H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.1 (q), 16.0 (q), 22.5 (t), 34.1 (t), 36.1 (t), 124.8 (d), 155.7 (s), 156.9 (s); ^{125}Te NMR (158 MHz, $CDCl_3$) δ 1607. Anal. Calcd for $C_8H_{13}NOTe$: C, 36.01; H, 4.91; N, 5.25%. Found: C, 36.00, H; 4.90; N, 5.28%.

4c (R^1 = *t*-C_4H_9, R^2 = Me): Pale Yellow Powder, mp 217.0-217.5 °C (decomp.); IR (KBr) 2952, 2908, 2866, 1564, 1465, 1363, 1125, 967, 897, 697, 451 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.41 (9H, s), 2.14 (3H, s), 7.00 (1H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 16.1 (q), 32.3 (q), 41.5 (s), 122.5 (d), 155.6 (s), 168.1 (s). (Lit.,[5c] 180-185 °C (decomp.), IR (KBr) 2953, 2912, 2865, 1565, 1466, 1424, 1389, 1370, 1361, 1337, 1243, 1231, 1202, 1125, 1030, 1001, 967, 896, 842, 828, 794, 760, 756, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.96 (1H, s), 2.17 (3H, s), 1.42 (9H, s); ^{13}C DEPTq NMR (125.8 MHz, CD_2Cl_2) δ 16.0, 32.1, 41.5, 122.7, 156.4, 168.9. HRMS calcd. for $C_8H_{14}ON^{129}Te$: *m/z* 270.0138 (M^+-H). Found: *m/z* 270.0122.)

4d (R^1 = *n*-C_4H_9, R^2 = H): Yellow oil; MS (*m/z*) 255 (M^+; bp, ^{130}Te), 253 (M^+; 92%, ^{128}Te), 251 (M^+; 56%, ^{126}Te), 250 (M^+; 22%, ^{125}Te), 249 (M^+; 14%, ^{124}Te), 247 (M^+; 7%, ^{122}Te); IR (neat) 2954, 2868, 2857, 1561, 1477, 1103, 1081, 744 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.90 (3H, t, *J* = 7.5 Hz), 1.38 (2H, sext, *J* = 7.5 Hz), 1.63 (2H, quint, *J* = 7.5 Hz), 2.86 (2H, t, *J* = 7.5 Hz), 7.12 (1H, d, *J* = 4.0 Hz), 8.31 (1H, d, *J* = 4.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.1 (q), 22.4 (t), 34.1 (t), 36.3 (t), 120.9 (d), 148.3 (d), 159.8 (s); ^{125}Te NMR (158 MHz, $CDCl_3$) δ 1639. HRMS Calcd for $C_7H_{11}NOTe$: *m/z* 254.9903. Found: *m/z* 254.9902.

4e (R^1 = C_6H_5, R^2 = H): Pale yellow powder, mp 217.8-218.1 °C (decomp.); MS (FAB^+, *m/z*) 274 (M^+-1; ^{130}Te, 29%), 272(M^+-1; ^{128}Te, 18%); IR (KBr) 1658, 1618, 1399, 1305, 1098, 1021, 836, 718, 694 cm^{-1}. Anal. Calcd for C_9H_7NOTe: C, 39.63; H, 2.59; N, 5.14%. Found: C, 39.62; H, 2.70; N, 5.13%.

4f (R^1 = Me, R^2 = H): Grayish powder, mp 203.4-203.7 °C (decomp.); IR (KBr) 1563, 1479, 1139, 1103, 1037, 801, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.55 (3H, s), 7.12 (1H, d, *J* = 3.5 Hz), 8.32 (1H, dd, *J*

= 3.5, 1.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.5 (q), 122.1 (d), 148.9 (d), 154.3 (s); ^{125}Te NMR (157 MHz, $CDCl_3$) δ 1654. HRMS Calcd for C_4H_5NOTe: *m/z* 212.9433. Found: *m/z* 212.9432.

A Typical Procedure for Deoxygenation of Isotellurazole *Te*-Oxide Oligomer 4a (R^1 = C_6H_5, R^2 = Me) by Treating with Ph_3P and I_2. A CH_2Cl_2 solution of Ph_3P (183 mg, 0.698 mmol, 2.0 equiv.) was treated with I_2 (89 mg, 0.349 mmol, 1.0 equiv.) at 0 °C for 30 min, and then isotellurazole *Te*-oxide oligomer **4a** (R^1 = C_6H_5, R^2 = Me, 100 mg, 0.349 mmol) was treated with the reaction mixture at 0 °C for 3 h. The reaction was then quenched by addition of saturated aqueous Na_2SO_3 solution, and the reaction mixture was extracted with $CHCl_3$. The organic layer was washed with water and was dried over anhydrous Na_2SO_4 powder. After removing the organic solvent *in vacuo*, the crude product was subjected to purification by using column chromatograph on silica gel to isolate isotellurazole **5a** (77 mg, yield 82%) as pale yellow solid.

5a (R^1 = C_6H_5, R^2 = Me): Pale yellow needles, mp 147.6-148.0 °C (Lit.,[2b,3c] 147.5-148.0 °C).

5b (R^1 = *n*-C_4H_9, R^2 = Me): Pale yellow oil; MS (*m/z*) 253 (M^+; bp, ^{130}Te), 251 (M^+; 93%, ^{128}Te), 249 (M^+; 57%, ^{126}Te), 248 (M^+; 22%, ^{125}Te), 247 (M^+; 14%, ^{124}Te), 245 (M^+; 7%, ^{122}Te); IR (neat) 2954, 2862, 1552, 1454, 1328, 831 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (3H, t, *J* = 7.5 Hz), 1.44 (2H, sext, *J* = 7.5 Hz), 1.66 (2H, quint, *J* = 7.5 Hz), 2.43 (3H, s), 2.96 (2H, td, *J* = 7.5 Hz, 1.0 Hz), 7.62 (1H, t, *J* = 1.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.1 (q), 22.3 (t), 23.2 (q), 34.5 (t), 38.4 (t), 128.9 (d), 171.8 (s), 182.4 (s); ^{125}Te NMR (158 MHz, $CDCl_3$) δ 1610. HRMS calcd for $C_8H_{13}NTe$: *m/z* 253.0110. Found: *m/z* 253.0110.

5c (R^1 = *t*-C_4H_9, R^2 = Me): Colorless needles; mp 55.5-56.0 °C; MS (*m/z*) 253 (M^+; bp, ^{130}Te), 251 (M^+; 92%, ^{128}Te), 249 (M^+; 56%, ^{126}Te), 248 (M^+; 22%, ^{125}Te), 247 (M^+; 14%, ^{124}Te), 245 (M^+; 8%, ^{122}Te); IR (KBr) 2955, 2923, 2854, 1552, 1455, 1361, 1317, 833, 712, 565 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (9H, s), 2.42 (3H, s), 7.60 (1H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.9 (q), 33.8 (q), 39.8 (s), 132.7 (d), 176.8 (s), 188.5 (s); ^{125}Te NMR (158 MHz, $CDCl_3$) δ 1642; HRMS Calcd for $C_8H_{13}NTe$: *m/z* 253.0110. Found: *m/z* 253.0106.

5d (R^1 = *n*-C_4H_9, R^2 = H): Colorless needles; mp 44.5-45.0 °C; MS (*m/z*) 239 (M^+; bp, ^{130}Te), 237 (M^+; 91%, ^{128}Te), 235 (M^+; 58%, ^{126}Te), 234 (M^+; 22%, ^{125}Te), 233 (M^+; 15%, ^{124}Te), 231 (M^+; 8%, ^{122}Te); IR (KBr) 2928, 2881, 2863, 1548, 1461, 1444, 1418, 1246, 792, 532 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (3H, t, *J* = 7.5 Hz), 1.45 (2H, sext, *J* = 7.5 Hz), 1.68 (2H, quint, *J* = 7.5 Hz), 3.03 (2H, td, *J* = 7.5, 1.0 Hz), 7.64 (1H, dt, *J* = 2.0, 1.0 Hz), 9.71 (1H, d, *J* = 2.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9 (q), 22.4 (t), 36.0 (t), 36.5 (t), 134.8 (d), 168.5 (d), 176.9 (s); ^{125}Te NMR (158 MHz, $CDCl_3$) δ 1677; HRMS Calcd for $C_7H_{11}NTe$: *m/z* 238.9954. Found: *m/z* 238.9953.

5e (R^1 = C_6H_5, R^2 = H): Pale yellow Powder, mp 134.8-135.5 °C; IR (KBr) 1534, 1441, 1420, 1261, 815, 751, 684, 565, 407 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.41 (3H, m), 7.48-7.50 (2H, m), 8.03 (1H,

s), 9.95 (1H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.9 (d), 129.4 (d), 129.5 (d), 132.2 (d), 138.1 (s), 169.3 (d), 173.1 (s). Anal. Calcd for C_9H_7NTe: C, 42.10; H, 2.75; N, 5.46%. Found: C, 42.08; H, 2.90; N, 5.46%.

5f (R^1 = Me, R^2 = H): Colorless needles; mp 99.0-99.5 °C (decomp.); MS (*m/z*) 198 (M^++1; bp, ^{130}Te); IR (KBr) 1549, 1433, 1253, 1128, 796 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.75 (3H, d, *J* = 1.0 Hz), 7.62 (1H, dq, *J* = 2.0, 1.0 Hz), 9.68 (1H, d, *J* = 2.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.0 (q), 137.1 (d), 168.1 (s), 168.4 (d); ^{125}Te NMR (158 MHz, $CDCl_3$) δ 1712. HRMS calcd for C_4H_6NTe: *m/z* 197.9562 ($M+H^+$). Found: *m/z* 197.9563.

REFERENCES AND NOTES

1. (a) V. Bertini and F. Lucchesini, *Synthesis*, 1982, 681; (b) R. Neidlein and D. Knecht, *Helv. Chim. Acta*, 1987, **70**, 1076; (c) T. Chivers, X. Gao, and M. Parvez, *Inorg. Chem.*, 1996, **35**, 9; (d) E. H. Morkved, M. V. Lakshmikantham, and M. P. Cava, *Tetrahedron Lett.*, 1996, **37**, 9149; (e) K. Badyal, M. Herr, W. R. McWhinnie, T. A. Hamor, and K. Paxton, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1998, **141**, 221; (f) D. Rajagopal, M. V. Lakshmikantham, E. H. Morkved, and M. P. Cava, *Org. Lett.*, 2002, **4**, 1193; (g) A. F. Cozzolino, I. Vargas-Baca, S. Mansour, and A. H. Mahmoudkhani, *J. Am. Chem. Soc.*, 2005, **127**, 3184; (h) A. F. Cozzolino and I. Vargas-Baca, *J. Organomet. Chem.*, 2007, **692**, 2654; (i) K. Shimada, *Science of Synthesis, Knowledge Updates*, 2010, 2010/1, 405, and the references cited therein.
2. (a) F. Lucchesini and V. Bertini, *Synthesis*, 1983, 824; (b) F. Lucchesini, V. Bertini, and A. De Munno, *Tetrahedron*, 1984, **40**, 931; (c) F. Lucchesini, V. Bertini, A. De Munno, M. Pocci, N. Picci, and M. Liguori, *Heterocycles*, 1987, **26**, 1587; (d) W. D. Pfeiffer, *Science of Synthesis*, 2002, **11**, 1005, and the references cited therein; (e) K. Shimada, *Science of Synthesis, Knowledge Updates*, 2010, **2010/1**, 467, and the references cited therein.
3. (a) K. Shimada, S. Oikawa, and Y. Takikawa, *Chem. Lett.*, 1992, 1389; (b) K. Shimada, S. Oikawa, H. Nakamura, and Y. Takikawa, *Chem. Lett.*, 1995, 135; (c) K. Shimada, A. Moro-oka, A. Maruyama, H. Fujisawa, T. Saito, R. Kawamura, H. Kogawa, M. Sakuraba, Y. Takata, S. Aoyagi, Y. Takikawa, and C. Kabuto, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 567.
4. K. Shimada, Y. Takata, Y. Osaki, A. Moro-oka, H. Kogawa, M. Sakuraba, S. Aoyagi, Y. Takikawa, and S. Ogawa, *Tetrahedron Lett.*, 2009, **50**, 6651.
5. (a) J. Kuebel, P. J. Elder, H. A. Jenkins, and I. Vargas-Baca, *J. Chem. Soc., Dalton Trans.*, 2010, **39**, 11126; (b) P. C. Ho, L. M. Lee, H. Jenkins, J. F. Britten, and I. Vargas-Baca, *Can. J. Chem.*, 2016, **94**, 453; (c) P. C. Ho, P. Szydlowski, J. Sinclair, P. J. Elder, J. Kübel, C. Gendy, L. M. Lee, H. Jenkins, J. F. Britten, D. R. Morim, and I. Vargas-Baca, *Nat. Commun.*, 2016, **7**, 11299.

6. (a) G. A. Olah, B. Gupta, and S. C. Narang, *Synthesis*, 1978, 137; (b) Z. Paryzek and R. Wydra, *Tetrahedron Lett.*, 1984, **25**, 2601; (c) X.-Y. Lu and X.-C. Tao, *Youji Huaxue*, 1987, **5**, 376; (d) S. Kikuchi, H. Konishi, and Y. Hashimoto, *Tetrahedron*, 2005, **61**, 3587; (e) T. Sideris and P. Ioannou, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2006, **181**, 1017; (f) K. Bahrami and Md. M. Khodaei, *Chem. Lett.*, 2007, **36**, 1324; (g) Y. Jang, K.-T. Kim, and H.-B. Jeon, *J. Org. Chem.*, 2013, **78**, 6328.
7. K. Shimada, S. Oikawa, H. Nakamura, A. Moro-oka, M. Kikuchi, A. Maruyama, T. Suzuki, H. Kogawa, Y. Inoue, Y. Gong, S. Aoyagi, and Y. Takikawa, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 899.