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Selective Formation of Trichloro(2-oxoalkyl)telluriums and Dichlorobis(2-oxoalkyl)telluriums from Tellurium Tetrachloride and Enol Silyl Ethers

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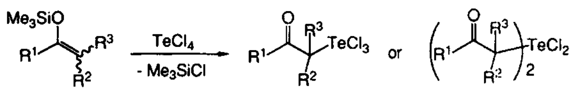
ABSTRACT

The reactions of $TeCl_4$ with 1 or 2 equivalents of enol silyl ethers yielded trichloro(2-oxoalkyl)telluriums or dichlorobis(2-oxoalkyl)telluriums, respectively, in high yields. Stepwise addition of two different enol silyl ethers to $TeCl_4$ in CH_2Cl_2 led to the selective formation of unsymmetrical dichlorobis(2-oxoalkyl)telluriums.

Trichloro(2-oxoalkyl)telluriums (**1**) and dichlorobis(2-oxoalkyl)telluriums (**2**) deposit metallic tellurium when heated or exposed to light and have attracted attention as potential thermal and photosensitive recording materials [1]. The general method for the preparation of **1** and **2** reported so far is the reaction of $TeCl_4$ with ketones in refluxing chloroform, which was investigated by Morgan and co-workers in the 1920s [2]. But, unfortunately, there are serious drawbacks arising from poor regioselectivities and restrictive limitations of this reaction. For example, 2-butanone reacts with $TeCl_4$ not only at the 1-position but also at the 3-position and, furthermore, gives a mixture of **1** and **2** [3].

In the course of our study on the chemical behavior of α-telluro carbonyl compounds [4], a new, efficient method for their preparation was needed. Since $TeCl_4$ adds to carbon–carbon unsaturated bonds [5] and since the reaction of $TeCl_4$ with ketones is proposed to involve the addition of $TeCl_4$ to their enol forms [2], we envisaged that $TeCl_4$ would react with enol silyl ethers (**3**) to afford **1** or **2**, as shown in Equation 1. The reaction was found to proceed under mild conditions, in comparison with that of $TeCl_4$ with the parent ketones, to give **1** or **2** selectively, depending on the amount of **3** used [6,7]. The equilibrium between **1** and **2** was also examined.



(1)

3 **1** **2**

A stoichiometric amount of 3,3-dimethyl-2-trimethylsiloxy-1-butene (**3e**) was added at 0°C to a $CDCl_3$ suspension of $TeCl_4$ in an NMR tube. The resulting homogeneous solution was kept at 25°C, and the reaction was monitored by ^1H NMR using dioxane as an internal standard. The signals of **3e** soon disappeared, and new peaks assignable to **1e** and **2e** were observed. It should be noted that **2e** initially formed was converted gradually to **1e**. For example, a ca. 4/1 mixture of **1e** and **2e**, obtained by the reaction of **3e** with $TeCl_4$ in $CDCl_3$ at 25°C for 30 minutes, gave only **1e** after 1 hour. This may indicate that **3e** reacts rapidly with both $TeCl_4$ and

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Dedicated to Prof. James Cullen Martin on the occasion of his sixty-fifth birthday.

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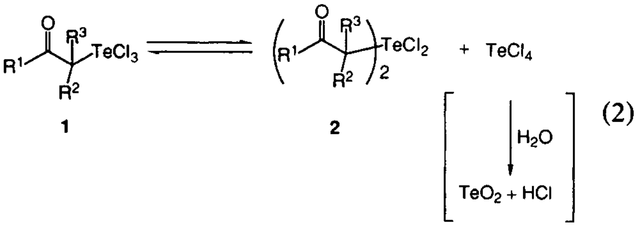
initially formed **1e** to give **1e** and **2e**, respectively, and that, thus formed, **2e** reacts slowly with remaining $TeCl_4$ to yield **1e**. The latter process was confirmed by a separate experiment using isolated **2e**, which afforded a quantitative yield of **1e** by the reaction with a stoichiometric amount of $TeCl_4$ at 25°C for 3 hours. A variety of trichloro(2-oxoalkyl)telluriums were obtained as a white solid or a colorless oil by the reaction of $TeCl_4$ with a stoichiometric amount of **3** in CH_2Cl_2 at 25°C for 2 hours (Table 1). Trichloro(2-oxoalkyl)telluriums (**1**) are very susceptible to moisture. When a few drops of water were added at 25°C to the $CDCl_3$ solution of 0.34 mmol of **1e**, an exothermic reaction took place and white precipitates were formed immediately to afford **2e** in 92% yield [8]. This would be explained by Equation 2. Under dry conditions, the equilibrium is biased to the left but shifts to the right in the presence of water driven by the irreversible reaction of $TeCl_4$ with water to form TeO_2 which deposits from the reaction medium. In contrast to **1e**, **2e** is stable toward water. For example, **2e** was recovered unchanged after treatment with 1N aqueous HCl at 25°C for 24 hours.



(2)

When 2.2 equiv of **3** was added to $TeCl_4$ in CH_2Cl_2 at 0°C and the mixture was stirred at 25°C for 2 hours, dichlorobis(2-oxoalkyl)tellurium (**2**) was obtained as the sole product. The ^1H NMR analysis of the resulting mixture showed no contamination of **1**, and column chromatography of the crude products on silica gel gave **2** as a white solid or a colorless oil in good yields (Table 1). It is noteworthy that **2** having secondary α-carbons, which could not be formed selectively by the direct reaction of ketones with $TeCl_4$ [3], could be prepared by this reaction in high yields (entries 10 and 11). Unfortunately, an attempt for the preparation of **2l** under similar conditions failed, resulting in the formation of only **1l**, probably due to a steric effect [9].

When $TeCl_4$ was allowed to react with an enol silyl ether in CH_2Cl_2 and then with another one, we could successfully obtain unsymmetrical dichlorobis(2-oxoalkyl)telluriums, as shown in Equation 3. The stepwise addition of 1 equiv each of the two enol silyl ethers, i.e., **3e** followed by **3b** or **3k**, afforded **2m** or **2n** in excellent yields. The ^1H NMR measurement of the crude mixture showed that contamination by symmetrical dichlorobis(2-oxoalkyl)telluriums (**2b**, **2e**, and **2k**, which could be expected to be formed) was less than 1%. These unsymmetrical dichlorobis(2-oxoalkyl)telluriums are kinetically stable, and no disproportionation was observed when **2n** was dissolved in $CDCl_3$ and the solution was kept at room temperature for 48 hours.

In summary, $TeCl_4$ was found to react with enol silyl ethers under mild conditions to give trichloro(2-oxoalkyl)telluriums (**1**) and dichlorobis(2-oxoalkyl)telluriums (**2**). By use of this method, a variety of **1** and **2** could be obtained selectively in excellent yields. The synthetic utility of this method has been demonstrated especially by the successful preparation of unsymmetrical dichlorobis(2-oxoalkyl)telluriums carrying secondary α-carbon(s), which could not be obtained by the direct reaction of ketones with $TeCl_4$.

EXPERIMENTAL

Instruments and Materials

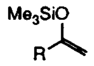
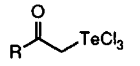
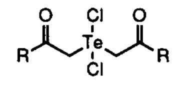
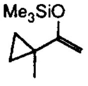
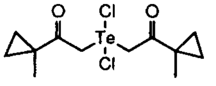
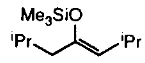
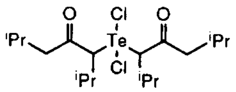
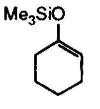
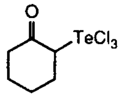
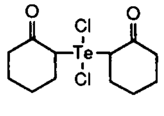
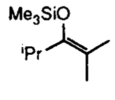
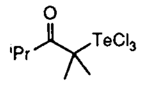
The ^1H NMR spectra were recorded on a JEOL JNM-GSX-270 (270 MHz) spectrometer using Me_4Si as an internal reference. The ^{13}C NMR spectra were taken on a JEOL JNM-GSX-270 (68 MHz) spectrometer. The IR spectra were recorded on a Perkin-Elmer Model 1600 spectrometer. Melting points were determined on a Yanagimoto Micro Melting Point apparatus and not corrected. Mass spectra were obtained on a JEOL JMS-DX303 instrument. The relative intensity of the ion involving Te and/or Cl represents the recorded peak height that appeared at the mass number calculated using ^{130}Te and/or ^{35}Cl, and the overlap of the ion(s) having different isotopes was not corrected.

Dichloromethane was washed with water, dried over $MgSO_4$, and distilled from CaH_2. Pentane was dried over CaH_2. Tellurium tetrachloride (99.9%) was purchased from Wako Pure Chemical Industries, Ltd. (Japan), and handled under dry Ar. Enol silyl ethers were prepared according to the literature [10] and purified by distillation.

A Typical Procedure for the Synthesis of Trichloro(2-oxoalkyl)telluriums (**1**)

To a suspension of $TeCl_4$ (1.2 mmol, 323 mg) in CH_2Cl_2 (6 mL) at 0°C was added dropwise **3e** (1.2 mmol, 207 mg). After the solution had been stirred at room temperature for 2 hours, the solvent was removed under reduced pressure to give a white solid. It was washed with pentane at −78°C and dried in vacuo to give **1e** as a white solid: 1.1 mmol (366 mg), 92%. The NMR spectral data of **1e** were in accord with the reported values [3] and showed essentially high purity without contamination of **2e** [8].

TABLE 1 Synthesis of Trichloro(2-oxoalkyl)telluriums (**1**) and Dichlorobis(2-oxoalkyl)telluriums (**2**)

entry	3	1, % yield[a]	2, % yield[a]
			
1	**3a** (R = Me)	**1a** 76 (84)	**2a** 90
2	**3b** (R = *n*-heptyl)	**1b** 82 (90)	**2b** 95
3	**3c** (R = *i*-Bu)		**2c** 92
4	**3d** (R = *i*-Pr)	**1d** 79 (88)	**2d** 87
5	**3e** (R = *t*-Bu)	**1e** 92 (97)	**2e** 93
6	**3f** (R = 1-adamantyl)		**2f** 93
7	**3g** (R = Ph)	**1g** 87 (92)	**2g** 97
8	**3h** (R = *p*-MeOC$_6$H$_4$)		**2h** 96
9	 **3i**		 **2i** 86
10	 **3j**		 **2j** 79
11	 **3k**	 **1k** 95 (96)	 **2k** 91
12	 **3l**	 **1l** 94 (99)	

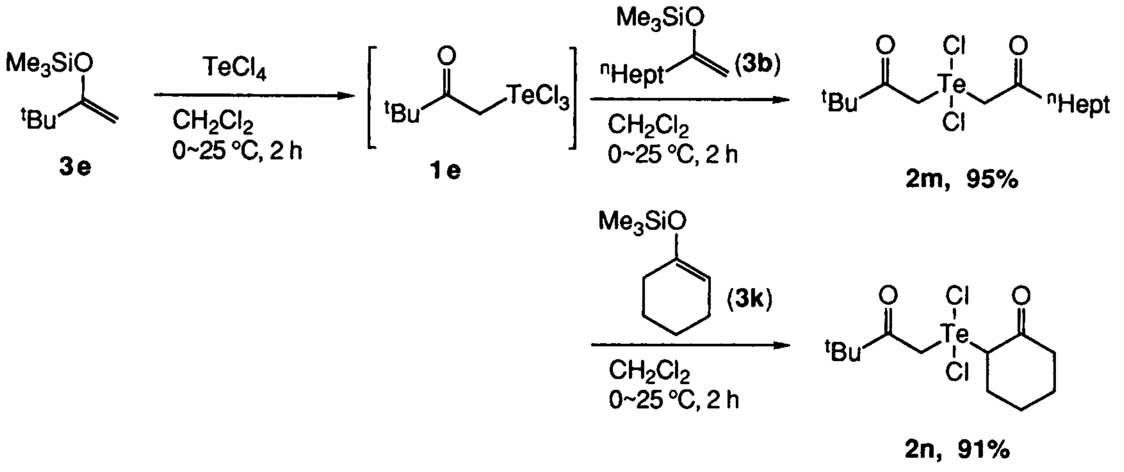
[a] Isolated yield (NMR yield).

Trichloro(2-oxopropyl)tellurium (**1a**) [3]. Oil; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 5.34 (s, 2H), 2.51 (s, 3H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 209.65, 80.65, 29.89.

Trichloro(2-oxononyl)tellurium (**1b**). Oil; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 5.27 (s, 2H), 2.72 (t, 2H, J = 7.4 Hz), 1.62–1.69 (m, 2H), 1.25 (bs, 8H), 0.84–0.86 (m, 3H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 212.58, 79.17, 42.79, 31.36, 28.70, 28.64, 23.58, 22.41, 13.94.

Trichloro(3-methyl-2-oxobutyl)tellurium (**1d**) [3]. Oil; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 5.37 (s, 2H), 2.84–2.92 (m, 1H), 1.27 (d, 6H, J = 6.8 Hz); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 216.38, 79.23, 41.26, 17.71.

Trichloro(3,3-dimethyl-2-oxobutyl)tellurium (**1e**) [3]. Mp 113–114°C (Ref. [11], 114–115°C); ^{1}H NMR (CDCl$_3$, 270 MHz) δ 5.44 (s, 2H), 1.30 (s, 9H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 218.92, 79.39, 45.20, 26.07.



(3)

Trichloro(2-oxo-2-phenylethyl)tellurium (**1g**) [12]. Oil; ^{1}H NMR (CDCl$_3$, 270 MHz) 7.95–8.00 (m, 2H), 7.56–7.62 (m, 3H), 5.84 (s, 2H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 200.10, 137.28, 130.40, 129.40, 128.63, 79.00.

Trichloro(1-oxo-2-cyclohexyl)tellurium (**1k**) [13]. Mp 142°C (Ref. [13], 140–143°C); ^{1}H NMR (CDCl$_3$, 270 MHz) δ 5.34 (dd, 1H, J = 7.8, 12.2 Hz), 2.40–3.02 (m, 6H), 1.72–1.80 (m, 2H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 214.57, 88.19, 41.41, 27.52, 24.85, 24.47.

Trichloro(1,1,3-trimethyl-2-oxobutyl)tellurium (**1l**) [3]. Oil; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 3.00 (heptet, 1H, J = 6.9 Hz), 2.45 (s, 6H), 1.25 (d, 6H, J = 6.9 Hz); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 225.15, 92.74, 36.74, 22.57, 19.07.

A Typical Procedure for the Synthesis of Dichlorobis(2-oxoalkyl)telluriums (2)

To a suspension of TeCl$_4$ (2.8 mmol, 754 mg) in CH$_2$Cl$_2$ (14 mL) at 0°C was added dropwise **3e** (6.2 mmol, 1.07 g). The solution was stirred at room temperature for 2 hours, and then the solvent was removed under reduced pressure to give a crude product. By flash column chromatography on silica gel using CH$_2$Cl$_2$ as an eluent, **2e** was obtained in pure form: 1.03 g (2.6 mmol), 93%.

Dichlorobis(2-oxopropyl)tellurium (**2a**) [3]. Mp 125.5–126°C (Ref. [11], 126–128°C); ^{1}H NMR (CDCl$_3$, 270 MHz) δ 4.67 (s, 4H), 2.42 (s, 6H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 200.93, 59.58, 30.74.

Dichlorobis(2-oxononyl)tellurium (**2b**). Mp 42–43°C. Anal. calcd for $C_{18}H_{34}Cl_2O_2Te$: C, 44.95; H, 7.13. Found: C, 44.67; H, 7.12. IR (KBr) 2929, 2854, 1693, 1467, 1399, 1358, 1220, 1047 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 4.65 (s, 4H), 2.63 (t, 4H, J = 7.4 Hz), 1.60–1.72 (m, 4H), 1.29 (bs, 16H), 0.88 (t, 6H, J = 6.8 Hz); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 203.16, 58.40, 43.09, 31.57, 28.93, 28.89, 23.76, 22.55, 14.04; MS (EI) m/e (relative intensity) 447 (M$^+$−Cl, 28), 341 (37), 127 (91), 57 (100).

Dichlorobis(4-methyl-2-oxopentyl)tellurium (**2c**) [3]. Mp 95–96°C (Ref. [11], 95°C); ^{1}H NMR (CDCl$_3$, 270 MHz) δ 4.62 (s, 4H), 2.50 (d, 4H, J = 7.0 Hz), 2.21 (m, 2H), 0.98 (d, 12H, J = 6.7 Hz); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 202.62, 59.24, 51.70, 25.19, 22.49.

Dichlorobis(3-methyl-2-oxobutyl)tellurium (**2d**) [3]. Mp 92–93°C (Ref. [11], 90°C); ^{1}H NMR (CDCl$_3$, 270 MHz) δ 4.73 (s, 4H), 2.77 (septet, 2H, J = 6.7 Hz), 1.22 (d, 12H, J = 6.7 Hz); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 206.60, 57.66, 40.97, 17.91.

Dichlorobis(3,3-dimethyl-2-oxobutyl)tellurium (**2e**) [3]. Mp 195–196°C dec (Ref. [11], 191–192°C); ^{1}H NMR (CDCl$_3$, 270 MHz) δ 4.86 (s, 4H), 1.25 (s, 18H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 208.45, 57.41, 44.08, 29.41.

Dichlorobis(2-(1-adamantyl)-2-oxoethyl) tellurium (**2f**). Mp 194–195°C dec. Anal. calcd for $C_{24}H_{34}Cl_2O_2Te$: C, 52.12; H, 6.20. Found: C, 52.43; H, 6.45. IR (KBr) 2902, 2849, 1684, 1450, 1365, 1268, 1226, 1007 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 4.80 (s, 4H), 2.10 (bs, 6H), 1.68–1.89 (m, 24H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 207.94, 57.18, 46.39, 38.18, 36.22, 27.69; MS (EI) m/e (relative intensity) 519 (M$^+$–Cl, 5), 484 (8), 377 (9), 342 (3), 135 (100).

Dichlorobis(2-oxo-2-phenylethyl)tellurium (**2g**) [13]. Mp 193–194°C dec (Ref. [14], 186–187°C); ^{1}H NMR (CDCl$_3$, 270 MHz) δ 8.03 (m, 4H), 7.52–7.69 (m, 6H), 5.31 (s, 4H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 192.19, 135.01, 134.36, 129.39, 129.13, 58.05.

Dichlorobis(2-(4-methoxyphenyl)-2-oxoethyl) tellurium (**2h**) [13]. Mp 193–195°C dec (Ref. [13], 190°C); ^{1}H NMR (DMSO-d_6, 270 MHz) δ 8.04 (d, 4H, J = 8.8 Hz), 7.12 (d, 4H, J = 8.8 Hz), 5.39 (s, 4H), 3.87 (s, 6H); ^{13}C NMR (DMSO-d_6, 68 MHz) δ 191.83, 164.39, 131.85, 127.76, 114.30, 55.76, 54.01.

Dichlorobis(2-(1-methylcyclopropyl)-2-oxoethyl)tellurium (**2i**). Mp 167°C dec. Anal. calcd for $C_{12}H_{18}Cl_2O_2Te$: C, 36.70; H, 4.62. Found: C, 37.14; H, 4.73. IR (KBr) 2966, 2930, 1655, 1461, 1437, 1339, 1320, 1284, 1193, 1076, 1057, 999, 850, 836 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 4.67 (s, 4H), 1.43 (bs, 10H), 0.96–0.97 (m, 4H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 204.22, 57.77, 27.23, 19.94, 19.61; MS (EI) *m/e* (relative intensity) 359 (M$^+$–Cl, 85), 324 (9), 297 (76), 262 (16), 227 (17), 185 (28), 97 (22), 83 (100).

Dichlorobis(1-isopropyl-4-methyl-2-oxopentyl)-tellurium (**2j**). Oil; a 1/1 mixture of diastereomers; IR (neat) 2960, 2873, 1701, 1467, 1391, 1367, 1031, 734 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 4.44 (d, 1H, J = 5.9 Hz), 4.39 (d, 1H, J = 6.4 Hz), 2.72–2.81 (m, 2H), 2.54 (d, 2H, J = 6.8 Hz), 2.49 (d, 2H, J = 7.4 Hz), 2.15–2.25 (m, 2H), 1.27 (d, 6H, J = 6.8 Hz), 0.87–0.98 (m, 18H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 206.19, 205.90, 77.66, 76.88, 29.50, 28.82, 24.35, 24.19, 23.86, 23.81, 22.62, 22.54, 20.51, 20.45; MS (EI) *m/e* (relative intensity) 447 (M$^+$–Cl, 12), 412 (3), 341 (29), 306 (19), 200 (80), 165 (79), 109 (70), 83 (100).

Dichlorobis(1-oxo-2-cyclohexyl)tellurium (**2k**). Oil; a 1/1 mixture of diastereomers; IR (neat) 2938, 2864, 1694, 1447, 1422, 1355, 1298, 1229, 1123, 1051, 1019, 962, 891, 851, 824, 659 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 4.69 (t, 1H, J = 7.9 Hz), 4.45 (dd, 1H, J = 6.3, 12.7 Hz), 1.70–2.73 (m, 16H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 205.57, 205.54, 70.20, 69.71, 41.69, 41.37, 30.70, 30.53, 25.81, 25.64, 25.45, 25.34; MS (EI) *m/e* (relative intensity) 359 (M$^+$–Cl, 41), 324 (9), 297 (80), 262 (28), 227 (9), 97 (100), 69 (71).

Dichloro(3,3-dimethyl-2-oxobutyl)(2-oxononyl)-tellurium (**2m**). Mp 38–41°C. Anal. calcd for $C_{15}H_{28}Cl_2O_2Te$: C, 41.05; H, 6.43. Found: C, 40.88; H, 6.38. IR (KBr) 2922, 2854, 1686, 1466, 1368, 1194, 1053, 997 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 4.87 (s, 2H), 4.62 (s, 2H), 2.63 (t, 2H, J = 7.3 Hz), 1.63–1.68 (m, 2H), 1.24–1.32 (m, 17H), 0.84–0.87 (m, 3H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 208.53, 203.14, 58.71, 56.82, 43.93, 43.06, 31.44, 28.81, 28.76, 26.26, 23.63, 22.42, 13.93; MS (EI) *m/e* (relative intensity) 405 (M$^+$–Cl, 4), 363 (45), 299 (35), 264 (17), 57 (100).

Dichloro(3,3-dimethyl-2-oxobutyl)(1-oxo-2-cyclohexyl)tellurium (**2n**). Mp 143–144°C dec. Anal. calcd for $C_{12}H_{20}Cl_2O_2Te$: C, 36.51; H, 5.11. Found: C, 35.95; H, 5.02. IR (KBr) 2970, 2936, 2870, 1688, 1477, 1466, 1447, 1427, 1367, 1351, 1300, 1190, 1131, 1052, 996 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 4.75 (dd, 1H, J = 6.8, 12.7 Hz), 4.65 (d, 1H, J = 15.1 Hz), 4.41 (d, 1H, J = 15.1 Hz), 2.69–2.81 (m, 2H), 2.43–2.56 (m, 2H), 2.16–2.20 (m, 2H), 1.67–1.83 (m, 2H), 1.24 (s, 9H); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 208.38, 205.08, 71.65, 56.34, 44.18, 41.12, 29.88, 26.40, 25.58, 24.94; MS (EI) *m/e* (relative intensity) 361 (M$^+$–Cl, 74), 299 (72), 264 (16), 97 (63), 57 (100).

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[7] Similar reactions of $ArTeCl_3$ with enol silyl ethers have been reported. (a) I. D. Sadekov, A. A. Maksimenko, B. B. Rivkin, *Zh. Org. Khim.*, *14*, 1978, 874; *Chem. Abstr.*, *89*, 1978, 42667. (b) H. A. Atefani, J. V. Comasseto, N. Petragnani, *Synth. Commun.*, *17*, 1987, 443. Very recently, $(ROC(O)CH_2)_2TeCl_2$ has been prepared by the reaction of $TeCl_4$ with corresponding ketene silyl acetals. (c) R. Tamura, H. Shimizu, N. Ono, N. Azuma, H. Suzuki, *Organometallics*, *11*, 1992, 954. One example of the reaction of $TeCl_4$ with an enol silyl ether has appeared in Ref. [7a], where 1-phenyl-1-trimethylsiloxyethylene afforded dichlorobis(2-oxo-2-phenylethyl)tellurium (**2g**) in a moderate yield (63%).

[8] Column chromatography of **1e** on silica gel resulted in hydrolysis to give **2e**.

[9] Even in refluxing chloroform, **3l** gave only **1l** and prolonged reaction time (>5 hours) caused the deposition of metallic tellurium.

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