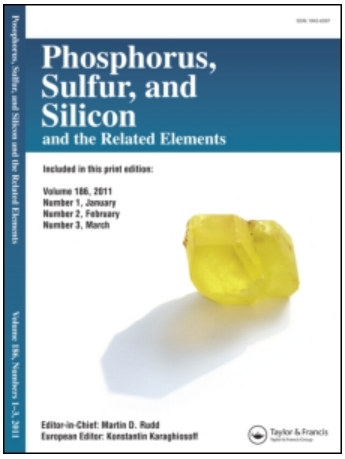

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Te-1-Acylmethyl and *Te*-1-Iminoalkyl Telluroesters: Synthesis and Thermolysis Leading to 1,3-Diketones and *O*-Alkenyl and *O*-Imino Esters

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Te-1-ACYLMETHYL AND *Te*-1-IMINOALKYL TELLUROESTERS: SYNTHESIS AND THERMOLYSIS LEADING TO 1,3-DIKETONES AND *O*-ALKENYL AND *O*-IMINO ESTERS

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A series of* Te-*1-acylmethyl carbotelluroates was prepared in good isolated yields from the reaction of potassium carbotelluroates with α-haloketones in acetonitrile. Thermolysis of the telluroesters afforded vinyl esters in 20−50% yields, while treatment of the carbotellurorates with potassium t-butanolate led to 1,3-diketones in 30−75% yields with the liberation of black tellurium. The reaction of potassium carbotelluroates with α-haloaceto oximes gave O-acyl oximes in 50−70% yields via Te-1-iminomethylcarbotelluroates.

Keywords 1,3-Diketones; detelluration; *O*-acyl iminoesters; *Te*-1-acylmethyl carbotelluroates; telluroesters; thermolysis

INTRODUCTION

1,3-Diketones have been widely used as important starting compounds for the synthesis of natural organic compounds. In 1971, Roth et al. reported the alkylative coupling via sulfide contraction of *S*-1-acylmethyl carbothioates to be a general method for the synthesis of enolizable β-dicarbonyl compounds.[1] In this reaction, trivalent phosphorous compounds as desulfurization agents have been used in the presence of a base such as potassium *tert*-pentanolate at 50−80°C. Deselenation reactions of *Se*-1-acylmethyl carboselenoates were found to proceed in the presence of an equimolar amount of the base at room temperature under mild conditions to afford 1,3-diketones in good yields.[2] The 1,3-diketone synthesis using *Te*-1-acylmethyl telluroesters is expected to proceed under more mild conditions. To the best of our knowledge, the synthesis of *Te*-1-acylmethyl telluroesters has not yet been described, most likely due to the difficulty of their synthesis and purification. We have established a method for preparing alkali metal carbotelluroates, which are important starting

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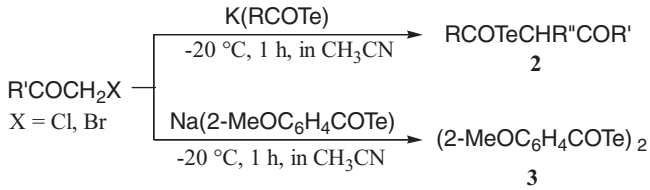
compounds for the synthesis of telluroesters.[3] The preparation of *Te*-α-functionalized-alkyl telluroesters using alkali metal carbotelluroates has also not yet been reported.[4] We present here the synthesis of *Te*-1-acylmethyl and *Te*-1-iminomethyl carbotelluroates, as well as the thermolysis and base treatment leading to 1,3-diketones and vinyl esters, respectively.

RESULTS AND DISCUSSION

Initially, the reaction conditions for the synthesis of *Te*-1-acylmethyl carbotelluroates **2** were examined using sodium 2-methoxybenzenecarbotelluroate and phenacyl bromide. These reactions resulted in the formation of di(2-methoxybenzoyl) ditelluride **3**. The reaction with potassium 2-methoxybenzenecarbotelluroate instead of the sodium salt in acetonitrile at –20°C for 1 h afforded the expected *Te*-phenacyl 2-methoxybenzenecarbotelluroate **2o** in good yield (Scheme 1).

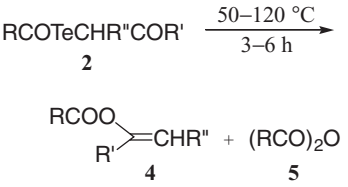


	R	R'	R"	Yield, %
2a	Et	*t*-Bu	H	86
2b	*i*-Pr	*t*-Bu	H	94
2c	*n*-Bu	4-BrC_6H_4	H	78
2d	Ph	Me	H	83
2e		Me	Me	83
2f		Et	H	66
2g		*t*-Bu	H	90
2h		Ph	H	97
2i		Ph	Me	81
2j		4-BrC_6H_4	H	86
2k		OEt	H	90
2l		NH_2	H	88
2m	4-MeC_6H_4	Ph	H	81
2n		4-BrC_6H_4	H	48
2o	2-$MeOC_6H_4$	Ph	H	93
2p	4-$MeOC_6H_4$	Me	H	78
2q		4-BrC_6H_4	H	91

Scheme 1

The reactions of other potassium carbotelluroates with α-haloketones under the conditions mentioned above led to *Te*-1-acylmethyl telluroesters **2a**−**2n** and **2p**−**2q** in yields of 48−97%.

In general, *Te*-alkyl carbotelluroates are labile thermally and towards oxygen. For example, upon exposure to air, compound **2h** gradually decomposed with the liberation of black tellurium to give 1-phenylethenyl benzoate **4h**. Under an argon atmosphere, heating of *Te*-phenacyl benezenecarbotelluroate **2h** at 80°C resulted in complete decomposition within 5 h to give 1-phenylethenyl benzoate **4h** and benzoic anhydride **5** (R = Ph) in yields of 32% and 10%, respectively, along with the liberation of elemental tellurium (Scheme 2).



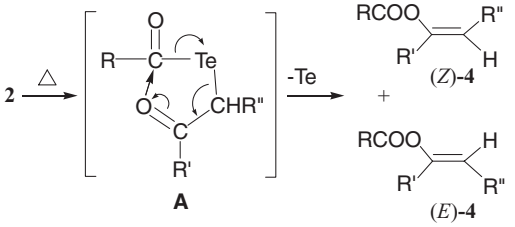
2 **4** **5**

	R	R'	R"	Yield, %
4a	Et	4-BrC_6H_4	H	45
4b	*i*-Pr	*t*-Bu	H	30
4c		Ph	H	40
4d		Ph	Me	42
4e	*n*-Bu	4-BrC_6H_4	H	36
4f	Ph	Et	H	45
4g		*t*-Bu	H	32
4h		Ph	H	32[a]
4i		4-BrC_6H_4	H	34
4j		Ph	Me	40
4k	4-MeC_6H_4	4-BrC_6H_4	H	32
4l	4-$MeOC_6H_4$	4-BrC_6H_4	H	20

[a]Compound **5** (R = Ph): 10%.

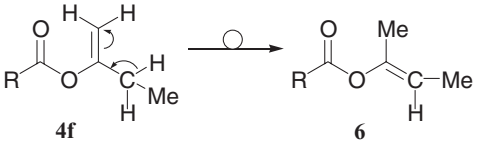
Scheme 2

Presumably, ethenyl esters **4** may be formed via the intramolecular attack of the α-carbonyl oxygen to the carbonyl carbon neighboring the tellurium atom (structure **A** in Scheme 3). In the case of **2f**, the formation of 1-methyl-1-propenyl ester **6** was observed along with 1-ethylethenyl ester **4f**, where the former resulted from the intramolecular 1,3 proton rearrangement in **4f** (Scheme 4).



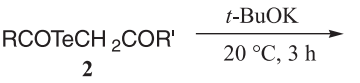
Scheme 3

Treatment of *S*-1-acylmethyl carbothioates with a base in the presence of a desulfurizing agent such as triphenylphosphine and lithium salts such as lithium perchlorate is known to afford 1,3-diketones in moderate yields.[1] In contrast, without triorganophosphines and lithium salts such as $LiClO_4$, *Se*-1-acylmethyl carboselenoates are converted



Scheme 4

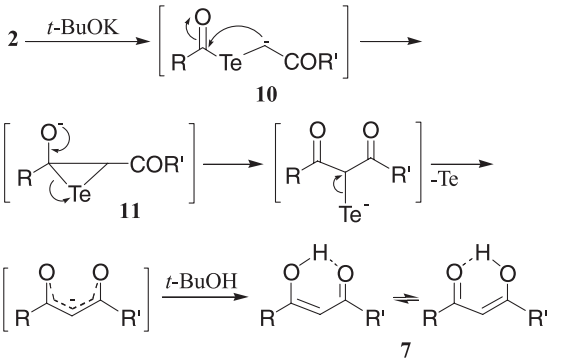
to 1,3-diketones upon treatment with potassium *tert*-pentanolate.[2] In the expectation of obtaining 1,3-diketones, we examined the reaction of *Te*-1-acylmethyl carbotelluroates **2** with a base under several conditions. Treatment of **2** with potassium *tert*-butanolate at 20°C for 24 h was found to lead to the corresponding 1,3-diketones **7** in 20−45% yields with the liberation of black tellurium (Scheme 5).



	R	R'	Yield, %
7a	Ph	Me	45
7b		Ph	35
7c	4-MeC_6H_4	Ph	26
7d		4-BrC_6H_4	23
7e	4-$MeOC_6H_4$	Me	28
7f		4-BrC_6H_4	36

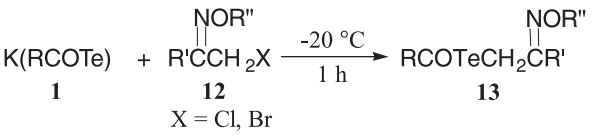
Scheme 5

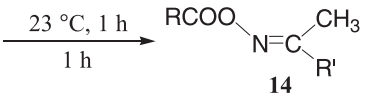
A possible mechanism for the formation of **7** is shown in Scheme 6, which involves the initial deprotonation of an active methylene group by potassium *tert*-butanolate, intramolecular attack of the resulting anion (**10**) on the carbonyl carbon atom, and finally elimination of the tellurium atom from the intermediately formed tellane (**11**) (Scheme 6).



Scheme 6

Previously, we reported the synthesis of 1,3-thiazoles from *N*-hydroxyiminomethyl carbodithioates.[5] To the best of our knowledge, *Te*-*N*-hydroxyiminomethyl carbotelluroates and 1,3-tellurazoles have not been described in the literature,[4a,c,d] In the expectation of obtaining these tellurium isologues, we investigated the reactions of **1** with α-halo oximes (Scheme 7).

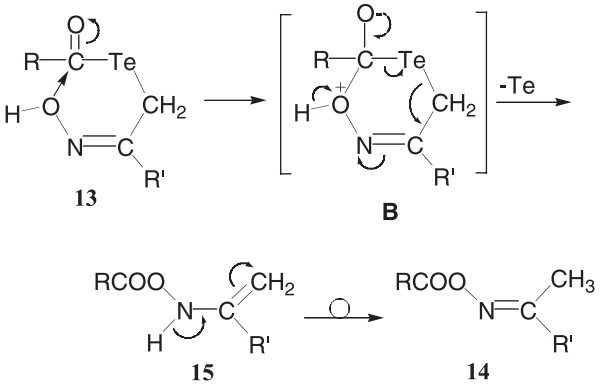




	R	R'	R"	**13** or **14** Yield, %
14a	Me	Me	H	71
14b	Ph	Me	H	60
14c	Ph	Ph	H	55
14d	Ph	4-BrC_6H_4	H	65
13e	Ph	Me	Me	87

Scheme 7

The reactions of potassium carbotelluroates **1** with acetoxime (**12**) proceeded at 0−20°C to form a mixture of *syn*- and *anti N*-1-hydroxyiminomethyl carbotelluroates (**13**) in good yields, which quickly decomposed at room temperature to give *syn*- and *anti-O*-acyl oximes (**14**).[6] One plausible mechanism for the formation of **14** is shown in Scheme 8, which involves detelluration of the cyclic intermediate **B**, which is formed by intramolecular attack of the hydroxy oxygen atom to the carbonyl carbon atom in **13** and subsequent 1,3-proton shift in the resulting *O*-1-ethenylamino ester (**15**) (Scheme 8).



Scheme 8

CONCLUSIONS

We have demonstrated that potassium carbotelluroates readily reacted with α-haloketons to afford *Te*-1-acylmethyl telluroesters in good yields. Thermolysis of the telluroesters leads to vinyl esters, while treatment of the telluroesters with potassium *tert*-butanolate results in the formation of 1,3-diketones in moderate yields. Moreover, we have described the one-pot conversion of *N*-1-hydroxyiminomethyl carbotelluroates, which are

readily obtained from the reaction of potassium carbotelluroates with acetoxime to *O*-acyl oximes. The operational simplicity and mild reaction conditions of these reactions not only offer some useful synthetic methods of vinyl esters, 1,3-diketones and *O*-acyl oximes, but also provide also a new C−C bond-forming reaction.

EXPERIMENTAL

All manipulations were carried out under argon. Melting points were determined with a Yanagimoto micro-melting point apparatus and are uncorrected. The IR spectra were measured with JASCO grating IR, Perkin-Elmer FT-IR 1640 and Shimazu FTIR spectrophotometers using KBr disc unless stated otherwise. ^{1}H (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were measured with a JEOL JNX-GX with tetramethylsilane as an internal standard. The mass spectra were obtained with a Hitachi RMU-6M high resolution mass spectrometer and a Shimadzu GCMS QP1000 and QP9020-DF (EI, mode) high resolution mass spectrometer. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University.

Materials

Tellurium (particles), which was powdered prior to use, sodium and potassium metals, phenacyl bromide, 4-bromophenacyl bromide, chloroacetophenone, 3-chloro-2-butanone, ethyl bromoacetate, 2-chloroacetoamide, and potassium *tert*-butanolate were purchased from Nacalai Tesque Co. (Kyoto, Japan). Sodium and potassium carbotelluroates were prepared by reacting the corresponding alkali metal with acyl chlorides according to the literature.[3] 2-Methoxybenzoyl, 4-methoxybenzoyl, and 4-methylbenzoyl chlorides were prepared according to the literature.[7] 3-Chloro-2,6-dimethoxybenzoyl chloride (purity: 99.9%) was supplied from Nippon Soda Co., Ltd.

Acetonitrile and dichloromethane were distilled under nitrogen atmosphere from phosphorus pentoxide. Ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen atmosphere. 2-Bromopropiophenone was prepared by bromination of propiophenone with bromine, according to the known method. α-Haloacetophenone oximes were prepared according to literature.[8]

Chloroacetone Oxime

Hydroxylamine hydrochloride (8.34 g, 40 mmol) and chloroacetone (3.70 g, 40 mmol) in ethanol (30 mL) were stirred at 20°C for 24 h. After removal of the solvent, the residue was extracted with ether (100 mL), followed by washing with water and drying over anhydrous sodium sulfate. Vacuum distillation gave 2.06 g (48%) of chloroacetone oxime (*syn*/*anti* = 90:10) as colorless liquid: bp 75−78°C/15 Torr.; IR (KBr): 3300, 1430, 1370, 1280, 1250, 1160, 1025, 890, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$) *anti*-conformer: $\delta = 2.02$ (s, CH_3), 4.09 (s, CH_2Cl); *syn*-conformer: $\delta = 2.04$ (s, CH_3), 4.29 (s, CH_2Cl); 9.70 (br, OH); ^{13}C NMR ($CDCl_3$) $\delta = 11.9$, 17.9 (CH_3), 36.3, 45.4 (CH_2Cl), 154.1, 154.8 (C=N).

α-Bromoacetophenone Oxime

Yield 1.80 g (56%) (*syn*/*anti* = 55:45); mp 90−92°C (colorless needles); IR (KBr) 3300, 1460, 1330, 1220, 1080, 955, 760, 690, 650 cm^{-1}; ^{1}H NMR ($CDCl_3$): *anti*-conformer:

$\delta = 4.43$ (s, CH_2Cl); *syn*-conformer: $\delta = 4.62$ (s, CH_2Cl); 9.55 (br, OH); ^{13}C NMR ($CDCl_3$): $\delta = 17.7$, 32.3 (CH_2Br), 126.2−133.3 (arom-ring), 154.3, 154.4 (C=N).

α,4′-Dibromoacetophenone Oxime

Yield 3.43 g (59%) (*syn*/*anti* = 55:45); mp 111−113°C (colorless needles); IR (KBr, neat): 1590, 1490, 1320, 1070, 960, 920, 830, 775, 730, 510 cm^{-1}; ^1H NMR ($CDCl_3$): *anti*-conformer: $\delta = 4.39$ (s, CH_2Cl); *syn*-conformer: $\delta = 4.58$ (s, CH_2Cl); 7.56 (s, 4H, arom-H), 8.96 (br, 1H, OH).

O-Methylchloroacetone Oxime

Yield 725 mg (24%) (*syn*/*anti* = 90:10); bp 53−55°C/30 Torr (colorless liquid); ^1H NMR ($CDCl_3$): *anti*-conformer: $\delta = 1.95$ (s, CH_3), 3.88 (s, CH_3O), 4.07 (s, CH_2Cl); *syn*-conformer: $\delta = 2.01$ (s, CH_3), 3.86 (s, CH_3O), 4.21 (s, CH_2Cl).

Typical procedures for the synthesis, thermolysis, and treatment of *Te*-α-ketoalkyl carbotelluroates (**2**) with *tert*-butanolate are described below. Compounds **2** were identified by comparison of their IR spectra with those of authentic samples prepared by the reaction of the corresponding sodium carbotelluroate with haloketones.

Te-2,2-Dimethylpropanoylmethyl Ethanecarbotelluroate (2a)

A solution of potassium ethanecarbotelluroate (0.99 mmol) in THF (5 mL) was added to a solution of 1-bromopinacolone (123 mg, 0.69 mmol) in acetonitrile (5 mL), and the mixture was stirred at –20°C for 1 h. Filtration of the black precipitate and evaporation of the solvent under reduced pressure (0°C/8 Torr) gave 170 mg (86%) of **2a** as yellow liquid: IR (KBr): 3000, 1700 (C=O), 1685 (C=O), 1475, 1360, 1280, 1150, 1000, 900, 670, 540 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.16$ (t, $J = 7.7$ Hz, 3H, CH_3), 1.23 (s, 9H, CH_3), 2.64 (q, $J = 7.7$ Hz, 2H, CH_2), 3.98 (s, 2H, CH_2Te); ^{13}C NMR ($CDCl_3$): $\delta = 9.0$ (CH_2Te), 15.3 (CH_3), 26.8 (CH_3), 44.6 (C−CO), 48.2 (CH_2CO), 202.6 (C=O), 213.2 (C=O); MS (CI): *m/z* = 286, 284, 282 (M+1).

Te-2,2-Dimethylpropanoylmethyl 1-Metylethanecarbotelluroate (2b)

Similarly to **2a**, the reaction of potassium benzenecarbotelluroate (1.78 mmol) with 1-bromopinacolone (165 mg, 0.92 mmol) gave 260 mg (94%) of **2b** as yellow liquid: IR (KBr, neat): 3100, 2950, 16600 (C=O), 1595 (C=O), 1580, 1450, 1360, 1230, 1200, 1170, 860, 760, 680, 660, 595 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.37$ (s, 3H, CH_3), 3.94 (s, 2H, CH_2Te); ^{13}C NMR ($CDCl_3$): $\delta = 14.9$ (CH_2Te), 18.1 (CH_3), 26.8 (CH_3), 44.6 (C−CO), 52.0 (CH_2CO), 207.8, 213.1 (C=O); MS (CI): *m/z* = 301, 299, 297 (M+1), 101 ($CH_2COC_4H_9$).

Te-4-Bromophenacyl 1-Butanecarbotelluroate (2c)

Similarly to **2a**, a solution of potassium 1-butanecarbotelluroate (1.06 mmol) in THF (5 mL) was added to a solution of 4-bromophenacyl bromide (208 mg, 0.75 mmol) in acetonitrile (5 mL), and the mixture was stirred at –20°C for 1 h. Filtration of the black

precipitate and evaporation of the solvent under reduced pressure (0°C/8 Torr) gave 240 mg (78%) of *Te*-4-bromophenacyl 1-butanecarbotelluroate **2c** as yellow liquid. IR (KBr): 3000, 2900, 1660 (C=O), 1580, 1270, 1070, 1010, 845, 745 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta =$ 0.92 (t, $J = 7.7$ Hz, 3H, CH_3), 1,38 (m, 2H, CH_2), 1.65 (m, 2H, CH_2), 2.66 (t, $J = 7.7$ Hz, 2H, CH_2CO), 4.32 (s, 2H, CH_2Te), 7.47−7.74 (m, 4H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta =$ 13.6 (CH_3), 15.3 (CH_2Te), 21.7, 26.9, 54.5 (CH_2), 126−133.6 (arom. ring), 196.9, 201.2 (*C*=O); MS (CI) *m/z* 416, 414, 412 (M+1), 84 (C_4H_9CO).

Te-Acetylmethyl Benzenecarbotelluroate (2d)

Similarly to **2a**, the reaction of potassium benzenecarbotelluroate (1.78 mmol) with chloroacetone (115 mg, 1.25 mmol) gave 300 mg (83%) of **2d** as yellow liquid. IR (KBr, neat): 3100, 2950, 1660 (C=O), 1590 (C=O), 1580, 1450, 1360, 1200, 1170, 865, 760, 680, 660, 595 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.37$ (s, 3H, CH_3), 3.94 (s, 2H, CH_2Te), 7.42−7.73 (m, 5H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 20.2$ (CH_2Te), 27.6 (CH_3), 126.9, 129.0, 134.2, 141.8 (arom. ring), 194.0 (*C*=O), 205.7 (*C*OTe); MS (CI): *m/z* = 293, 291, 289 (M+1), 105 (C_6H_5CO); HRMS calcd. for $C_{10}H_{10}O_2Te$: 291.9743, found: 291.9748.

Te-1-Acetylethyl Benzenecarbotelluroate (2e)

Similarly to **2a**, the reaction of potassium 1-methylethanecarbotelluroate (1.18 mmol) with 1-bromo-2-butanone (125 mg, 0.83 mmol) gave 210 mg (83%) of **2e** as yellow liquid. IR (KBr, neat): 3000, 1690 (C=O), 1660 (C=O), 1575, 1440, 1200, 1170, 865, 760, 680, 660, 610, 590 cm^{-1}; ^1H NMR (CDCl): $\delta = 1.11$ (t, $J = 7.7$ Hz, 2H, CH_2), 3.95 (s, 2H, CH_2Te), 7.45−7.75 (m, 5H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 8.5$ (CH_2Te), 27.6 (CH_3), 126.9, 129.0, 143.2, 141.8 (arom. ring), 194.0 (*C*=O), 209.0 (*C*=O); MS (CI): *m/z* = 307, 305, 303 (M+1), 105 (C_6H_5CO).

Te-Propanoylmethyl Benzenecarbotelluroate (2f)

Similarly to **2a**, the reaction of potassium benzenecarbotelluroate (2.43 mmol) with 2-chloro-2-butanone (181 mg, 1.70 mmol) gave 340 mg (66%) of **2f** as yellow liquid. IR (KBr, neat): 3100, 2920, 1690 (C=O), 1660 (C=O), 1570, 1440, 1170, 1000, 860, 760, 680, 660, 590 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.89$ (d, $J = 7.7$ Hz, 9H, CH_3), 2.43 (s, 3H, CH_3), 4.39 (s, 2H, CH_2Te), 7.45−8.14 (m, 5H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 18.6$ (CH_2Te), 27.0 (CH_3), 34.8 *C*-CO), 126.9−142.3 (arom. ring), 195.3, 207.5 (C=O).

Te-2,2-Dimethylpropanoylmethyl Benzenecarbotelluroate (2g)

Similarly to **2a**, the reaction of potassium benzenecarbotelluroate (1.58 mmol) with 1-bromo-2-butanone (198 mg, 1.11 mmol) gave 330 mg (90%) of **2g** as yellow liquid. IR (KBr, neat): 3100, 2950, 1690 (C=O), 1660 (C=O), 1595, 1580, 1480, 1360, 1200, 990, 860, 760, 660, 610, 590 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.27$ (s, 9H, CH_3), 4.19 (s, 2H, CH_2Te), 7.45−7.73 (m, 5H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 16.7$ (CH_2Te), 27.0 (CH_3), 44.8 *C*-CO), 126.9, 129.1, 134.2, 142.6 (arom. ring), 195.6 (*C*=O), 213.3 (*C*=O); MS (CI): *m/z* = 335, 333, 331 (M+1), 105 (C_6H_5CO).

Te-Phenacyl Benzenecarbotelluroate (2h)

Similarly to **2a**, the reaction of freshly prepared potassium benzenexarbotelluroate (1.96 mmol) with phenacyl bromide (273 mg, 1.37 mmol) gave 470 mg (97%) of **2h** as yellow oil. IR (neat): 3070, 1655 (C=O), 1590, 1575, 1440, 1265, 1195, 1165, 995, 860, 750, 695, 670, 650, 580 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 4.55$ (s, 2H, CH_2Te), 7.35−8.03 (m, 10H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 16.6$ (*C*H_2Te), 126.8−141.8 (arom. ring), 194.5 (*C*=O), 197.5 (*C*=O); MS (CI): *m/z* = 356, 352 (M+1), 105 (C_6H_5CO); HRMS: calcd for $C_{15}H_{12}O_2Te$: 353.9899; found: 353.9878.

Te-1-Methylphenacyl Benzenecarbotelluroate (2i)

Similarly to **2a**, the reaction of potassium benzenecarbotelluroate (2.18 mmol) with 2-chloro-2-butanone (325 mg, 1.52 mmol) gave 450 mg (81%) of **2i** as yellow liquid. IR (KBr, neat): 3000, 2950, 1655 (C=O), 1590, 1580, 1445, 1340, 1225, 1070, 860, 755, 705, 590 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.13$, (3H, CH_3), 5.29 (2H, CH_2Te), 7.34−8.05 (m, 10H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 20.2$ (*C*HTe), 29.8 (*C*H_3), 126.8−141.9 (arom. ring), 195.3 (*C*=O), 199.3 (*C*=O); MS (CI): *m/z* = 368, 366, 364 (M+1), 105 (C_6H_5CO).

Te-4-Bromophenacyl Benzenecarbotelluroate (2j)

Similarly to **2a**, the reaction of freshly prepared potassium benzenecarbotelluroate (1.63 mmol) with 4-bromophenacyl bromide (362 mg, 1.30 mmol) gave a yellow solid. Chromatographic separation on silica gel column [dichloromethane/hexane (1:1), Rf = 0.30, the second eluent] gave 480 mg (86%) of **2j** as yellow crystals. M.p. 60−64°C; IR (neat): 3000, 1655 (C=O), 1630, 1580, 1480, 1440, 1400, 1265, 1200, 1070, 1000, 870, 785, 760, 680, 665, 598 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 4.52$ (s, 2H, CH_2Te), 7.42−8.14 (m, 9H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 16.3$ (*C*H_2Te), 127.0−141.9 (arom. ring), 194.7 (*C*=O), 197.0 (*C*=O).

Te-Ethoxycarbonylmethyl Benzenecarbotelluroate (2k)

Similarly to **2a**, the reaction of potassium benzenecarbotelluroate (1.87 mmol) with ethyl bromoacetate (218 mg, 1.31 mmol) and chromatographic separation on silica gel column [dichloromethane/hexane (1:1), Rf = 0.33, the second eluent] gave 380 mg (90%) of **2k** as yellow liquid. IR (KBr, neat): 3000, 2950, 1715 (C=O), 1660 (C=O), 1580, 1445, 1245, 1090, 1030, 860, 760, 680, 660, 595 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.24$ (t, $J = 7.7$ Hz, 3H, CH_3), 3.81 (s, 2H, CH_2Te), 4.16 (q, $J = 7.7$ Hz, 2H, CH_2O), 7.42−7.73 (m, 5H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 9.2$ (*C*H_3), 13.9 (*C*H_2Te), 61.3 (*C*H_2O), 127.0, 129.1, 134.2, 142.1 (arom. ring), 172.8 (*C*OO), 193.8 (*C*OTe); MS (CI): *m/z* = 323, 321, 319 (M+1), 105 (C_6H_5CO).

Te-Aminocarbonylmethyl Benzenecarbotelluroate (2l)

Similarly to **2a**, the reaction of potassium benzenecarbotelluroate (1.28 mmol) with 2-chloroacetoamide (82 mg, 0.90 mmol) gave 230 mg (88%) of **2l** as yellow crystals. IR (KBr, neat): 3460 (NH), 3350 (NH), 3250, 1660 (C=O), 1640, 1615, 1175, 1160, 860, 770, 660, 590 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.63$ (s, 2H, CH_2Te), 5.71 (s, 1H, NH), 7.42−7.74

(m, 5H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 10.5$ (CH_2Te), 127.0, 129.3, 134.6, 142.3 (arom. ring), 175.3 (*C*ON), 198.4 (*C*OTe); MS (CI): *m/z* = 294, 292, 290 (M+1), 105 (C_6H_5CO).

Te-Phenacyl 4-Methylbenzenecarbotelluroate (2m)

Similarly to **2a**, the reaction of freshly prepared potassium 4-methylbenzenecarbotelluroate (1.49 mmol) with phenacyl bromide (207 mg, 1.04 mmol) and chromatographic separation on silica gel column [dichloromethane/hexane (1:1), Rf = 0.27, the second eluent] gave 310 mg (81%) of **2m** as yellow oil. IR (neat): 3000, 1660 (C=O), 1635, 1580, 1450, 1310, 1270, 1205, 1170, 870, 780, 760, 610, 590 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.37$ (s, 3H, CH_3), 4.56 (s, 2H, CH_2Te), 7.23−8.05 (m, 9H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 16.4$ (CH_2Te), 21.8 (CH_3), 127.2−145.6 (arom. ring), 193.9 (*C*=O), 198.1 (*C*=O); HRMS: calcd. for $C_{11}H_{12}O_2Te$: 368.0056; found: 368.0048.

Te-4-Bromophenacyl 4-Methylbenzenecarbotelluroate (2n)

Similarly to **2a**, the reaction of freshly prepared potassium benzenecarbotelluroate (1.93 mmol) with 4-bromophenacyl bromide (536 mg, 1.93 mmol) and chromatographic separation on silica gel column [dichloromethane/hexane (1:1), Rf = 0.35, the second eluent] gave 590 mg (48%) of **2n** as yellow crystals. Mp 73−78°C; IR (KBr): 3000, 1660 (C=O), 1630, 1590, 1580, 1560, 1390, 1300, 1260, 1195, 1170, 1140, 1060, 990, 870, 770, 600, 580 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.34$ (s, 3H, CH_3), 4.48 (s, 2H, CH_2Te), 7.20−7.89 (m, 8H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 16.0$ (CH_2Te), 21.7 (CH_3), 127.1−145.6 (arom. ring), 193.5 (*C*=O), 196.9 (*C*=O); MS (CI): *m/z* = 447, 445, 443 (M+1), 119 ($CH_3C_6H_4CO$).

Te-Phenacyl 2-Methoxybenzenecarbotelluroate (2o)

Similarly to **2a**, the reaction of freshly prepared potassium 2-methoxybenzenecarbotelluroate (0.92 mmol) with phenacyl bromide (128 mg, 0.65 mmol) and chromatographic separation on silica gel column [dichloromethane/hexane (1:1), Rf = 0.31, the second eluent] gave 230 mg (93%) of **2o** as yellow crystals. Mp 75−80°C; IR (neat): 3000, 1660 (C=O), 1630, 1480, 1280, 880, 770, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 3.92$ (s, 3H, CH_3O), 4.44 (s, 2H, CH_2Te), 6.96−8.05 (m, 9H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 27.2$ (CH_2Te), 55.2 (CH_3O), 112.1, 121.1, 127.0, 128.4, 128.5, 128.8, 129.1, 132.9, 134.9, 159.6 (arom. ring), 195.0 (*C*=O), 199.1 (*C*=O); MS (CI): *m/z* = 384, 382, 380 (M+1), 1135 ($CH_3OC_6H_4CO$). HRMS: calcd. for $C_{15}H_{12}O_2Te$: 353.9899; found: 353.9878.

Te-Acetylmethyl 4-Methoxybenzenecarbotelluroate (2p)

Similarly to **2a**, the reaction of potassium 4-methoxybenzenecarbotelluroate (1.37 mmol) with chloroacetone (88 mg, 0.96 mmol) gave 240 mg (78%) of **2p** as yellow liquid. IR (KBr, neat): 3100, 2950, 1660 (C=O), 1630, 1570, 1410, 1350, 1260, 1210, 1160, 1175, 1160, 860, 770, 660, 590 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.37$ (s, 3H, CH_3), 3.87 (s, 3H, CH_3O), 3.92 (s, 2H, CH_2Te), 6.92−7.71 (m, 4H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta =$ 20.0 (CH_2Te), 27.6 (CH_3), 55.6 (CH_3O), 114.2−164.5 (arom. ring), 191.1 (*C*OMe), 206.3

(*C*OTe); MS (CI): *m/z* = 325, 323, 321 (M+1), 135 ($CH_3C_6H_4CO$); HRMS calcd. for $C_{11}H_{12}O_3Te$: 321.9848; found: 321.9864.

Te-4-Bromophenacyl 4-Methoxybenzenecarbotelluroate (2q)

Similarly to **2a**, the reaction of freshly prepared potassium 4-methoxybenzenecarbotelluroate (1.33 mmol) with 4-bromophenacyl bromide (258 mg, 0.93 mmol) and chromatographic separation on silica gel column [dichloromethane/hexane (1:1), Rf = 0.50, the second eluent] gave 160 mg (62%) of **2q** as yellow solid. Mp 93−96°C (yellow crystals); IR (neat): 3000, 1660 (C=O), 1635, 1595, 1580, 1570, 1505, 1260, 1170, 1030, 995, 880, 780, 610, 595 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 3.84 (s, 3H, CH_3O), 4.48 (s, 2H, CH_2Te), 6.90−7.90 (m, 8H, arom-H); ^{13}C NMR ($CDCl_3$): δ = 15.9 (*C*H_2Te), 55.6 (*C*H_3O), 114.0−164.7 (arom. ring), 191.5 (*C*=O), 197.1 (*C*=O); Anal: calcd. for $C_{16}H_{13}O_3BrTe$: C 41.71, H 2.84; Found: C 40.63, H 2.83.

Thermolysis of *Te*-α-Ketoalkyl Carbotelluroates (2) Leading to Vinyl Esters (4)

1-4-Bromophenylethenyl propanoate (4a). *Te*-4-bromophenacyl ethanecarbotelluroate **2a** (200 mg, 0.52 mmol) was heated under argon atmosphere at 80°C for 3 h. Ether (50 mL) was added, and the precipitate (black tellurium) was separated by filtration. Removal of the solvent and chromatography of the residue on silica gel column [dichloromethane/hexane (1:1), Rf = 0.43, the first eluent] gave 60 mg (45%) of **4a** as colorless oil. IR (KBr, neat): 3000, 2950, 1755 (C=O), 1640, 1585, 1485, 1250, 1140, 1090, 1005, 890, 830 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.24 (t, *J* = 7.3 Hz, 3H, CH_3), 2.54 (q, *J* = 7.3 Hz, 2H, CH_2), 5.04 (d, *J* = 7.3 Hz, 1H, C*H* = C), 5.44 (d, *J* = 2.2 Hz, 1H, C*H* = C), 7.30−7.48 (m, 4H, arom-H); ^{13}C NMR ($CDCl_3$): δ = 9.0 (*C*H_3), 27.7 (*C*H_2), 102 (*C*=*C*), 123.0, 126.5, 131.7, 133.6, 152.2 (arom. ring), 172.4 (*C*=O); MS (CI): *m/z* = 256, 254 (M+1); HRMS: calcd. for $C_{11}H_{11}O_2Br$: 253.9942; found: 253.9919.

3,3-Dimethyl-1-butenyl 1-methylbutanoate (4b). Similarly to **4a**, heating of *Te-2,2*-dimethylpropanoylmethyl 1-methylethanecarbo-telluroate **2b** (240 mg, 0.80 mmol) at 50−60°C for 3 h, and chromatographic separation on silica gel column [dichloromethane/hexane (1:1), Rf = 0.45, the first eluent] gave 40 mg (30%) of **4b** as colorless oil. IR (KBr, neat): 3010, 2930, 1750 (C=O), 1650, 1470, 1390, 1365, 1130, 1060, 1020, 880 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.10 (s, 9H, CH_3), 1.24 (d, *J* = 7.0 Hz, 6H, CH_3), 2.66 (1H, CH_3), 4.61 (d, *J* = 1.8 Hz, 1H, C*H*=C), 4.85 (d, *J* = 1.8 Hz, 1H, C*H*=C); ^{13}C NMR ($CDCl_3$): δ = 19.2 (*C*H_3), 27.8 (*C*H_3), 34.5 (*C*H), 36.2 (*C*CO), 98.6 (*C*=*C*), 162.6 (*C*=*C*), 175.1 (*C*=O); MS (CI): *m/z* = 171 (M+1); HRMS: calcd. for $C_{10}H_{18}O_2$: 170.1307; found: 170.1301.

1-Phenylethenyl 1-methylbutanoate (4c). Similarly to **4a**, heating of *Te*-phenacyl 1-methylethanecarbotelluroate **2c** (250 mg, 0.78 mmol) at 80−90°C for 5 h, and chromatographic separation on silica gel column [dichloromethane/hexane (1:1), Rf = 0.23, the first eluent] gave 60 mg (40%) of **4c** as colorless oil. IR (KBr, neat): 3000, 1745 (C=O), 1630, 1495, 1470, 1265, 1130, 760, 690 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.30 (6H, CH_3), 2.79 (1H, CH), 5.00 (d, *J* = 2.2 Hz, 1H, C*H*=C), 5.45 (d, *J* = 2.2 Hz, 1H, C*H*=C), 7.25−7.48 (m, 5H, arom-H); ^{13}C NMR ($CDCl_3$): δ = 19.0 (*C*H_3), 34.2 (*C*H), 101.9 (*C*=*C*),

124.9, 128.5, 134.6, 153.1 (arom. ring), 175.1 (*C*=O); MS (CI): *m/z* = 190 (M+1), 105 ($CH_2=CC_6H_5$); HRMS: calcd. for $C_{12}H_{14}O_2$: 190.0993; found: 190.1008.

1-Phenyl-1-methylethenyl 1-methylpropanoate (4d). Similarly to **4a**, heating of *Te*-1-methylphenacyl 1-methylethanecarbotelluroate **2d** (170 mg, 0.51 mmol) at 80−100°C for 5 h and chromatography on silica gel column [dichloromethane/hexane (1:1), Rf = 0.50, the first eluent] gave 50 mg (42%) of 1-(phenyl)-1-methylethenyl 1-methylpropanoate **4d** (*E/Z* = 6:94) as colorless oil. IR (KBr, neat): 3000, 1745 (C=O), 1460, 1440, 1230, 1130, 1060, 745, 680 cm^{-1}; ^1H NMR ($CDCl_3$): *Z*-**4d**: $\delta = 1.34$ (d, $J = 7.0$ Hz, 3H, CH_3), 1.69 (d, $J = 7.3$ Hz, 3H, CH_3C=C), 2.83 (m, 1H, CH), 5.87 (q, $J = 7.0$ Hz, 1H, C*H*=C), 7.28−7.40 (m, 5H, arom-H); *E*-**4d**: $\delta = 1.21$ (d, $J = 7.0$ Hz, 3H, CH_3), 1.82 (d, $J = 7.3$ Hz, 3H, CH_3C=C), 3.03 (m, 1H, CH), 5.52 (q, $J = 7.0$ Hz, 1H, C*H*=C), 7.27−7.40 (m, 5H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 11.5$ (*C*H_3), 19.2 (*C*H_3), 34.2 (*C*H), 112.5, 124.3, 128.0, 128.5, 135.3, 146.9 (arom. ring), 158.2 (*C*=*C*), 174.6 (*C*=O); MS (CI): *m/z* = 205 (M+1); HRMS: calcd. for $C_{13}H_{16}O_2$: 192.1150; found: 192.1144.

1-4′-Bromopheny-)ethenyl 1-pentanoate (4e). Similarly to **4a**, heating of *Te*-4-bromophenacyl 1-butanecarbotelluroate **2d** (220 mg, 0.50 mmol) at 80−90°C for 3 h. Chromatographic separation on silica gel column [dichloromethane/hexane (1:1), Rf = 0.43, the first eluent] gave 50 mg (36%) of **4e** as colorless oil and 30 mg (8%) of 4-bromoacetophenone **9g** as colorless crystals. **4e**: IR (KBr, neat): 3000, 1750 (C=O), 1640, 1595, 1495, 1480, 1255, 1225, 1140, 1090, 1010, 830 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.95$ (t, $J = 7.3$ Hz, 3H, CH_3), 1.40 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 2.53 (t, $J = 7.3$ Hz, 2H, CH_2CO), 5.03 (d, $J = 2.2$ Hz, 1H, C*H*=C), 5.43 (d, $J = 2.2$ Hz, 1H, C*H*=C), 7.30−7.48 (m, 4H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 13.7$ (*C*H_3), 22.3, 26.9, 34.0 (*C*H_2), 102.6 (*C*=*C*), 123.0, 126.5, 131.7, 133.6, 152.6 (arom. ring), 171.7 (*C*=O); MS (CI): *m/z* = 285, 283 (M+1), 85 (C_4H_9CO); HRMS: calcd. for $C_{13}H_{17}BrO_2$: 284.04119; found: 284.04107. **9g**: M.p. 50−52°C. The IR of **9g** was consistent with that of the authentic sample.

1-Ethyl-ethenyl Benzoate (4f) and 1-Methyl-1-propenyl Benzoate (6)

Similarly to **4a**, heating of *Te*-propanoylmethyl benzenecarbotelluroate **2f** (330 mg, 0.50 mmol) at 90−100°C for 5 h and chromatography on silica gel column [dichloromethane/hexane (1:1), Rf = 0.43, the first eluent] gave 80 mg (45%) of a mixture of **4f** and **6** (*E/Z* = 30:70) (**4f**/**6** = 60:40) as colorless oil. IR (KBr, neat): 3000, 2950, 1720 (C=O), 1600, 1450, 1260, 1175, 1110, 1070, 1030, 710 cm^{-1}; **4f**: ^1H NMR ($CDCl_3$): $\delta = 1.13$ (t, $J = 7.7$ Hz, 3H, CH_3), 2.35 (q, $J = 7.7$ Hz, 2H, CH_2), 4.83 (d, $J = 7.3$ Hz, C*H*=C), 4.85 (d, $J = 7.3$ Hz, 1H, C*H*=C), 7.44−8.13 (m, 4H, arom-H). **6** (*E/Z*): $\delta = 1.53$ (d, $J = 1.5$ Hz, 3H, CH3), 1.69 (q, $J = 6.6$ Hz, 3H, CH_3), 1.98 (q, $J = 1.5$ Hz, 3H, CH_3), 5.15 (d, $J = 1.5$ Hz, 1H, C*H*=C), 5.29 (q, $J = 5.5$ Hz, 1H, C*H*=C), 7.44−8.13 (m, 4H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 10.7$, 11.1, 19.5, 26.6 (*C*H_2, *C*H_3), 100.4−145.8 (*C* = *C*, arom. ring), 158.2 (*C* = C), 164.8 (*C*=O); MS (CI): *m/z* = 176 (M+1), 105 (C_6H_5CO); HRMS: calcd. for $C_{11}H_{11}O_2$: 176.08373; found: 176.08354.

3,3-Dimethyl-1-butenyl Benzoate (4g)

Similarly to **4a**, heating of *Te*-2,2-dimethylpropanoylmethyl benzenecarbotelluroate **2g** (280 mg, 0.84 mmol) at 150−160°C for 5 h and chromatography on silica gel column [dichloromethane/hexane (1:1), Rf = 0.60, the first eluent] gave 40 mg (32%) of **4g** as colorless oil. IR (KBr, neat): 3000, 2900, 1730 (C=O), 1650, 1600, 1450, 1280, 1260,

1140, 1020, 890, 830, 700 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 1.19$ (s, 3H, CH_3), 4.81 (d, $J =$ 2.2 Hz, 1H, C*H*=C), 4.99 (d, $J = 2.2$ Hz, 1H, C*H*=C), 7.48−8.12 (m, 5H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 28.0$ (*C*H_3), 36.5 (*C*-CO), 92.2 (C = C), 128.5, 130.0, 130.2, 133.2, 162.8 (arom. ring), 164.8 (*C*=O); MS (CI): *m/z* = 205 (M+1), 105 (C_6H_5CO); HRMS: calcd. for $C_{13}H_{16}O_2$: 204.1151; found: 204.1148.

1-Phenylethenyl Benzoate (4h)

Similarly to **4a**, heating of *Te*-phenacyl benzenecarbotelluroate **2h** (350 mg, 0.91 mmol) at 100−110°C for 5 h and chromatography on silica gel column [dichloromethane/hexane (1:1), Rf = 0.38, the first eluent] gave 40 mg (32%) of **4h** as colorless oil and 15 mg (10%) of benzoic anhydride **5a** colorless solid. **4h**: IR (KBr, neat): 3000, 2950, 1730 (C=O), 1640, 1600, 1490, 1450, 1240, 1100, 1070, 1030, 890, 830, 790, 710 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 5.16$ (d, $J = 2.2$ Hz, 1H, C*H*=C), 5.59 (d, $J = 2.2$ Hz, 1H, C*H*=C), 7.24−8.12 (m, 10H, arom-H); ^{13}C NMR ($CDCl_3$): δ = 12.3, 25.0−153.3 (*C*=*C*, arom. ring), 164.8 (*C*=O); MS (CI): *m/z* = 225 (M+1), 105 (C_6H_5CO); HRMS calcd. for $C_{15}H_{12}O_2$: 224.0832; found: 224.0816. **5a**: M.p. 39−41°C. The IR spectrum of **5a** was consistent with that of an authentic sample.

1-(4-Bromophenyl)ethenyl Benzoate (4i)

Similarly to **4a**, heating of *Te*-4-bromophenacyl benzenecarbotelluroate **2j** (260 mg, 0.30 mmol) at 90−100°C for 5 h and chromatography on silica gel column [dichloromethane/hexane (1:1), Rf = 0.44, the first eluent] gave 500 mg (34%) of **4i** as colorless oil. IR (KBr, neat): 3000, 2950, 1730 (C=O), 1640, 1590, 1480, 1450, 1240, 1170, 1090, 1060, 1020, 1010, 830, 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 5.20$ (d, $J =$ 2.2 Hz, 1H, C*H*=C), 5.58 (d, $J = 2.2$ Hz, 1H, C*H*=C), 7.26−8.15 (m, 9H, arom-H); MS (CI): *m/z* = 305, 303 (M+1), 185, 183 (CH_2=CC_6H_4Br); HRMS calcd. for $C_{15}H_{11}O_2Br$: 301.9942; found: 301.9928.

1-Phenyl-1-propenyl Benzoate (4j)

Similarly to **4a**, heating of *Te*-1-methylphenacyl benzenecarbotelluroate **2i** (450 mg, 1.22 mmol) at 90−100°C for 5 h and chromatography on silica gel column [dichloromethane/hexane (1:1), Rf = 0.57, the first eluent] gave 50 mg (40%) of **4j** (*E*/*Z* = 5:95) as colorless oil. IR (KBr, neat): 3100, 2950, 1725 (C=O), 1595, 1495, 1450, 1420, 1175, 1090, 1065, 1025, 750, 705 cm^{-1}; ^1H NMR ($CDCl_3$): (*Z*)-**4l**: $\delta = 1.76$ (d, $J = 7.0$ Hz, 3H, CH_3), 6.01 (q, $J = 7.0$ Hz, 1H, C*H*=C), 7.26−8.25 (m, 10H, arom-H); (*E*)-**4j**: δ = 1.88 (d, $J = 7.0$ Hz, 3H, CH_3), 5.68 (q, $J = 7.0$ Hz, 1H, C*H*=C), 7.26−8.25 (m, 10H, arom-H); ^{13}C NMR ($CDCl_3$) $\delta = 11.7$ (*C*H_3), 112.9, 124.4, 128.1, 128.7, 129.4, 130.2, 133.6, 135.1, 147.1 (*C*=*C*), 158.2 (*C*=*C*, arom. ring), 164.3 (*C*=O); MS (CI): *m/z* = 239 (M+1), 105 (C_6H_5CO); HRMS: calcd. for $C_{16}H_{14}O_2$: 238.09938; found: 238.09926.

1-(4-Bromophenyl)ethenyl 4-Methylbenzoate (4k)

Similarly to **4a**, heating of *Te*-phenacyl 4-methylbenzenecarbotelluroate **2m** (670 mg, 1.50 mmol) at 90−100°C for 6 h and chromatography on silica gel column

[dichloromethane/hexane (1:1), Rf = 0.37, the first eluent] gave 153 mg (32%) of **4k** as colorless crystals. IR (KBr, neat): 3000, 2950, 1720 (C=O), 1640, 1600, 1580, 1470, 1240, 1170, 1040, 1000, 880, 840, 740 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.43$ (s, 3H, CH_3), 5.17 (d, $J = 2.2$ Hz, 1H, C*H*=C), 5.56 (d, $J = 2.2$ Hz, 1H, C*H*=C), 7.28−8.07 (m, 9H, arom-H); MS (CI): *m/z* = 318, 316 (M+1), 119 ($CH_3C_6H_4CO$); HRMS calcd. for $C_{16}H_{13}O_3Br$: 316.00989; found: 316.0076.

1-(4-Bromophenyl)ethenyl 4-Methoxybenzoate (4l)

Similarly to **4a**, heating of *Te*-4-bromophenacyl 4-methoxybenzenecarbotelluroate **2q** (220 mg, 0.47 mmol) at 100−110°C for 5 h and chromatography on silica gel column [dichloromethane/hexane (1:1), Rf = 0.33, the first eluent] gave 40 mg (20%) of **4l** as colorless oil. IR (KBr, neat): 3000, 1720 (C=O), 1680, 1610, 1590, 1510, 1400, 1260, 1240, 1170, 1090, 1010, 830, 760 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.96$ (s, 3H, CH_3O), 5.19 (d, $J = 2.2$ Hz, 1H, C*H*=C), 5.55 (d, $J = 2.2$ Hz, 1H, C*H*=C), 6.90−8.20 (m, 8H, arom-H); MS (CI): *m/z* = 335, 333 (M+1), 135 ($CH_3OC_6H_4CO$); HRMS calcd for $C_{16}H_{13}O_3Br$: 332.0048; found: 332.0046; Anal calcd. for $C_{16}H_{13}O_3Br$: C, 60.59, H, 4.13; found: C, 60.95, H, 4.44.

Treatment of *Te*-α-Ketoalkyl Carbotelluroates (2) with Potassium *tert*-Butanolate Leading to 1,3-Diketone (7)

1-Phenyl-1,3-butanedione (7a). *tert*-Butanol (20 mL) containing potassium *tert*-butanolate (50 mg, 0.5 mmol) was added to *Te*-acetylmethyl benezenecarbotelluroate **2d** (100 mg, 0.5 mmol). The mixture was stirred at 20°C for 3 h under argon atmosphere and then ether (50 mL) was added. The insoluble part (black) was filtered, and the solvent was removed under reduced pressure. Chromatography of the resulting precipitate on silca gel [dichloromethane/hexane (1:1), Rf = 0.41, the first eluent] gave 25 mg (45%) of **7a** as colorless crystals. Mp 59−60°C (Lit; 57−59°C[2], Lit; 60−61°C[9]); IR (KBr, neat): 3000, 2950, 1700 (C=O), 1660 (C=O), 1260, 1020, 840, 760, 695 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.20$ (s, 3H, CH_3), 6.18 (s, 1H, C*H*=C), 7.45−7.89 (m, 5H, arom-H); MS (CI): *m/z* = 162 (M+1), 105 (C_6H_5CO); HRMS: calcd. for $C_{10}H_{10}O_2$: 162.0680; found: 162.0660.

1,3-Diphenyl-1,3-propanedione (7b). Similarly to **7a**, the reaction of *Te*-phenacyl benzenecarbotelluroate **2h** (150 mg, 1.33 mmol) with *tert*-butanolate (50 mg, 0.50 mmol), followed by separation using silica gel column chromatography [dichloromethane/hexane (1:1)], gave 50 mg (35%) of **7b** (Rf = 0.45, the first eluent) and 25 mg (45%) of acetophenone **9b** (Rf = 0.21, the second eluent) as colorless oil, respectively. **7b**: Mp 75−77°C (Lit; 75−78°C[10]); IR (KBr, neat): 3100, 2950, 1595 (C=O), 1310, 1230, 1000, 740, 680, 605 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 6.84$ (s, 1H, C*H*=C), 7.44−7.99 (m, 10H, arom-H), 16.87 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): $\delta = 93.2$ (*C*H_2), 127.2, 128.7, 132.4, 135.6 (arom-C), 185.8 (*C*=O); MS (CI): *m/z* = 223 (M+1), 105 (C_6H_5CO; HRMS: calcd for $C_{15}H_{12}O_2$: 224.0837; found: 224.0839. **9b**: M.p. 20°C. The m.p. and IR spectrum of **9b** were consistent with those of an authentic sample.

1-(4′-Methylphenyl)-3-phenyl-1,3-propanedione (7c). Similarly to **7a**, the reaction of *Te*-phenacyl 4-methylbenzenecarbotelluroate **2m** (310 mg, 1.33 mmol) with *tert*-butanolate (70 mg, 0.62 mmol), followed by separation using silica gel column chromatography [dichloromethane/hexane (1:1), Rf = 0.40, the first eluent], gave 20 mg (26%) of **7c** as colorless crystals: Mp 86−89°C. IR (KBr, neat): 3100, 2950, 1600 (C=O), 1540,

1530, 1480, 1300, 1230, 1180, 810, 765, 695, 680 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.43$ (s, 3H, CH_3), 6.83 (s, 1H, C*H*=C), 7.25−7.99 (m, 9H, arom-H), 16.91 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): $\delta = 21.7$ (*C*H_3), 92.9 (*C*H_2), 127.1−143.3 (arom-C), 185.2 (*C*=O), 186.1 (*C*=O); MS (CI): *m/z* = 239 (M+1), 119 ($CH_3C_6H_4CO$); HRMS: calcd for $C_{15}H_{12}O_2$: 224.0837; found: 224.0834.

1-(4-Bromophenyl-3-(4-methyl)phenyl-1,3-propanedione (7d). Similarly to **7a**, the reaction of *Te*-4-bromophenacyl 4-methylbenzenecarbotelluroate **2n** (1010 mg, 2.27 mmol) with *tert*-butanolate (254 mg, 2.27 mmol), followed by separation using silica gel column chromatography [dichloromethane/hexane (1:1)], gave 66 mg (23%) of **7d** (Rf = 0.35, the first eluent) and 30 mg (15%) of 4-bromoacetophenone **9g** (Rf = 0.10, the third eluent) as colorless crystals, respectively. **7d**: Mp 162−165°C; IR (KBr, neat): 3100, 2950, 1600 (C=O), 1580, 1480, 1300, 1225, 1210, 1070, 1010, 840, 780, 490 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.43$ (s, 3H, CH_3), 6.77 (s, 1H, C*H*=C), 7.27−7.89 (m, 8H, arom-H), 16.85 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): $\delta = 21.7$ (*C*H_3), 92.7 (*C*H_2), 127.1−143.5 (arom. ring), 184.0 *C* = O), 186.2 (*C*=O); MS (CI): *m/z* = 319, 317 (M+1), 119 ($CH_3C_6H_4CO$); HRMS: calcd. for $C_{16}H_{13}O_2Br$: 316.0098; found: 316.0081. **9g**: M.p. 50−52°C (Lit. 54°C[11]). The mp and IR spectrum of **9g** were consistent with those of an authentic sample.

1-(4′-Methoxy)phenyl-1,3-butanedione (7e). Similarly to **7a**, the reaction of *Te*-acetylmethyl 4-methoxybenzenecarbotelluroate **2p** (240 mg, 0.75 mmol) with *tert*-butanolate (84 mg, 0.75 mmol), followed by separation using silica gel column chromatography [dichloromethane/hexane (1:1)], gave **7e** (Rf = 0.52, the first eluent) and 40 mg (35%) of 4-methoxybenzoic acid **8** (R = 4-MeC_6H_4) (Rf = 0.31, the second eluent) as colorless crystals, respectively. **7e**: Mp 48−51°C; IR (KBr, neat): 3100, 2950, 1600 (C=O), 1260, 1180, 1020, 845, 770 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.17$ (s, 3H, CH_3), 3.86 (s, 3H, CH_3O), 6.12 (s, 1H, C*H*=C), 6.92−7.88 (m, 4H, arom-H), 16.32 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): $\delta = 25.3$ (*C*H_3), 55.3 (*C*H_3O), 95.8 (*C*H_2), 113.9, 127.6, 129.1, 163.1 (arom. ring), 189.2 (*C*=O), 191.6 (*C*=O); HRMS: calcd. for $C_{11}H_{12}O_3$: 192.0786; found: 192.0778. **8** (R = 4-$MeOC_6H_4$)**:** M.p. 181−184°C (Lit. 182−185°C[12]). The mp and IR spectrum of **8** (R = 4-MeC_6H_4) were consistent with those of an authentic sample.

1-(4-Bromophenyl)-3-(4-methoxyphenyl)-1,3-propanedione (7f). Similarly to **7a**, the reaction of *Te*-4-bromophenacyl 4-methoxybenzenecarbotelluroate **2q** (763 mg, 1.66 mmol) with *tert*-butanolate (186 mg, 1.66 mmol), followed by separation using silica gel column chromatography [dichloromethane/hexane (1:1)], gave 50 mg (36%) of **7f** (Rf = 0.35, the second eluent) and 30 mg (20%) of 4-methoxybenzoic acid **8** (R = 4-$MeOC_6H_4$) (Rf = 0.02, the third eluent) as colorless crystals, respectively. **7f**: Mp 150−153°C; IR (KBr, neat): 3100, 2950, 1600 (C=O), 1580, 1300, 1230, 1170, 1065, 1020, 1000, 840, 780 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 3.89$ (s, 3H, CH_3O), 6.74 (s, 1H, C*H*=C), 6.97−7.98 (m, 4H, arom-H), 16.96 (s, 1H, OH); ^{13}C NMR ($CDCl_3$): $\delta = 25.3$ (*C*H_3), 55.3 (*C*H_3O), 95.8 (*C*H_2), 113.9, 127.6, 129.1, 163.1 (arom. ring), 189.2 (*C*=O), 191.6 (*C*=O); MS (CI): *m/z* = 335, 333 (M+1), 135 ($CH_3C_6H_4CO$); HRMS: calcd. for $C_{16}H_{13}BrO_2$: 332.00481; found: 332.00446. **8** (R = 4-$MeOC_6H_4$): M.p. 181−184°C (Lit. 182−185°C[12]), the m.p. and IR spectrum were consistent with those of an authentic sample.

Typical Procedures for the Reaction of Potassium Benzenecarbotelluroates (1) (R = Phenyl) with α-Haloketo Oximes (12) Leading to *Te*-α-Iminopropyl Carbotelluroates (13) or *O*-Acylacetophenone Oximes (14)

***O*-Acetyl acetone oxime (14a).** A solution of chloroacetone oxime **12a** (120 mg, 1.11 mmol) in acetonitrile (5 mL) was added to the freshly prepared potassium methanecarbotelluroate (0.75 mmol) in tetrahydrofuran (5 mL) at –20°C under argon atmosphere. The mixture was stirred at this temperature for 1 h; the pink color of the potassium salt quickly changed to pale yellow. Filtration of the precipitate and removal of the solvent under reduced pressure at 0 to –5°C gave 190 mg of yellow oil (71% as *syn*/*anti*-*Te*-2-hydroxyiminopropyl methanecarbotelluroate **13a** (black tellurium quickly liberates at room temperature). Chromatography of this yellow oil on silica gel column [dichloromethane/hexane (2:1), Rf = 0.60, the first eluent] gave 80 mg (63%) of *O*-acetyl acetone oxime **14a** (*syn*/*anti* = 90:10) as colorless liquid. IR (KBr, neat): 2960, 2850, 1750 (C=O), 1370 (C=O), 1280, 1210, 1010, 940, 600 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.01$ (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 3.16 (s, 3H, CH_3O); ^{13}C NMR ($CDCl_3$): $\delta = 16.7$ (CH_3), 19.2 (CH_3O), 21.7 (CH_3), 163.6 ($C=N$), 168.6 (C=O); MS (CI): *m/z* = 102 (M+1), 105 (C_6H_5CO); HRMS: calcd. for $C_4H_7NO_2$: 101.04768; found: 101.04768.

***O*-Benzoyl acetone oxime (14b).** Similarly to **14a**, the reaction of potassium benzenecarbotelluroates (2.06 mmol) with α-bromoacetophenone oxime **12b** (155 mg, 1.44 mmol) gave 310 mg of yellow oil (71% as *Te*-2-hydroxyiminoacetophenone benzenecarbotelluroate **13b**; the yellow changed to colorless with liberation of black tellurium. Dichloromethane (5 mL) was added. Filtration of the precipitate, removal of the solvent, and chromatographic separation of the resulting residue on silica gel column (dichloromethane/hexane = 2:1, Rf = 0.51, the second eluent) gave 92 mg (60%) of *O*-benzoyl acetone oxime **14b** (*syn*/*anti* = 95:5) as colorless liquid: IR (KBr, neat): 3010, 1735 (C=O), 1600, 1450, 1375, 1280, 1250, 1090, 1060, 1030, 910, 820, 805 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.12$ (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 7.43−8.08 (m, 5H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 16.9$ (CH_3), 21.9 (CH_3), 128.4, 129.2, 129.4, 133.1 (arom. ring), 163.8 ($C=N$), 164.5 (C=O); MS (CI): *m/z* = 164 (M+1), 105 (C_6H_5CO); HRMS: calcd. for $C_9H_9NO_2$: 163.06333; found: 163.06325.

***O*-Benzoyl acetophenone oxime (14c).** Similarly to **14a**, the reaction of potassium benzenecarbotelluroates (1.31 mmol) with α-bromoacetophenone oxime **12c** (196 mg, 0.92 mmol) in acetonitrile (15 mL) gave 300 mg of yellow crystals (89%) as *Te*-acetophenone oxime benzenecarbotelluroate **13c**. Ether (50 mL) was added. Filtration of the insoluble precipitate (black), removal of the solvent, and chromatographic separation of the resulting residue on silica gel column (dichloromethane/hexane = 2:1, Rf = 0.52, the second eluent) gave 120 mg (55%) of *O*-benzoyl acetophenone oxime **14c** (*syn*/*anti* = 82:18) as colorless crystals. M.p 95−98°C; IR (KBr, neat): 3000, 1730 (C=O), 1440, 1310, 1230, 1050, 1010, 900, 755, 690 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.45$ (*anti*) / 2.13 (*syn*) (s, 3H, CH_3), 7.33−8.12 (m, 10H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 14.6$ (CH_3), 127.1, 134.8 (arom. ring), 163.6 ($C=N$), 163.7 (C=O); MS (CI): *m/z* = 226 (M+1), 105 (C_6H_5CO); HRMS: calcd. for $C_{14}H_{11}NO_2$: 225.07898; found: 225.07876.

***O*-Benzoyl 4-bromoacetophenone oxime (14d).** Similarly to **14c**, the reaction of potassium benzenecarbotelluroates (2.31 mmol) with α-4′-dibromoacetophenone oxime **12d** (473 mg, 1.62 mmol) gave 720 mg of yellow crystals (70−75°C, 98%) as *Te*-4-bromoacetophenone oxime benzenecarbotelluroate **13d**. Upon exposure to air, the yellow

color quickly disappeared with liberation of black tellurium. Chromatographic separation of the resulting residue on silica gel column (dichloromethane/hexane = 2:1, Rf = 0.50, the second eluent) gave 280 mg (65%) of *O*-benzoyl 4-bromoacetophenone oxime (**14d**) (*syn*/*anti* = 95:5) as colorless crystals. Mp 118−120°C; IR (KBr): 3000, 1730 (C=O), 1310, 1250, 1055, 920, 820, 690, 545 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.45 (*anti*), 2.52 (*syn*) (s, 3H, CH_3), 7.42−8.11 (m, arom-H); ^{13}C NMR ($CDCl_3$): δ = (*syn*/*anti* = 95 : 5) 14.1 (CH_3), 61.3 (CH_3O), 125.0−133.5 (arom. ring), 162.3 (C = N), 163.4 (C=O); MS (CI): *m/z* = 306, 305 (M+1), 105 (C_6H_5CO); HRMS: calcd. for $C_{14}H_{10}BrNO_2$: 302.989494; found: 302.98465.

***Te*-2-Methoxyiminopropyl benzenecarbotelluroate (13e).** A solution of freshely prepared potassium benzenecarbotelluroate (1.54 mmol) in THF (5 mL) was added to chloro-*O*-methoxyacetone oxime **12e** (131 mg, 1.08 mmol) in acetonitrile (5 mL) at –20°C, and the reaction mixture was stirred for 1 h; the red color of the potassium salt changed to pale yellow within 10 min. The insoluble parts (black Te, excess of K(PhCOTe), KCl) were separated by filtration. Removal of the solvent under reduced pressure gave 300 mg (87%) of *Te*-2-methoxyiminopropyl benzenecarbotelluroate **13e** (*anti*/*syn* = 90:10) as yellow oil. IR (KBr, neat): 2960, 2850, 1715 (C=O), 1660 (C=O), 1575, 1440, 1360, 1200, 1170, 1050, 910, 860, 835, 755, 680, 660, 590 cm^{-1}; ^1H NMR ($CDCl_3$): *anti*-**13e**: δ = 1.98 (s, 3H, CH_3), 3.86 (s, 3H, CH_3O), 3.73 (s, 2H, CH_2Te); *syn*-**13e**: δ = 2.03 (s, 3H, CH_3), 3.83 (s, 3H, CH_3O), 3.91 (s, 2H, CH_2Te), 7.40−7.74 (m, 5H, arom-H); ^{13}C NMR ($CDCl_3$): δ = 4.4, 15.1, 19.2 (CH_2, CH_3), 126.7, 128.3, 129.2, 129.4, 142.5 (arom. ring), 156.5 (C=N), 195.6 (C=O); MS (CI): *m/z* = 320, 318, 316 (M+1), 105 (C_6H_5CO). The IR spectrum was consistent with that of an authentic sample, which was prepared from the reaction of sodium benezenecarbotelluroate with chloro-*O*-methoxyacetone oxime.

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