A New General Method for the Preparation of Unsymmetrical Telluronium Salts

Yoshihiro Matano and Hitomi Suzuki*,†

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Nagao Azuma

Department of Chemistry, Faculty of General Education, Ehime University, Bunkyo-cho, Matsuyama 790-77, Japan

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A new general approach to a variety of unsymmetrical telluronium salts has been developed. Treatment of diaryltellurinyl difluorides **1** with silyl enol ethers **2** in the presence of $BF_3{\cdot}OEt_2$ gave (2-oxoalkyl)diaryltelluronium tetrafluoroborates **3** in quantitative yield. When a siloxycyclopropane, an allylsilane, a benzylstannane, an alkenylstannane, an alkynylsilane, or an arylstannane was used in place of compound **2**, the corresponding 3-oxoalkyl-, allyl-, benzyl-, alkenyl-, and alkynyldiaryltelluronium tetrafluoroborates as well as the unsymmetrically triarylated telluronium salt were obtained in good yields. The ^{125}Te chemical shifts of these compounds span over the range δ 645−755 ppm, which were in accordance with the onium nature of the tellurium center. An X-ray structural analysis of **3a** clearly showed that the central tellurium atom has a distorted-pyramidal structure with a weak coordinative interaction between the tellurium and carbonyl oxygen atoms. The telluronium salt $[Ph_2TeCH_2CH_2C(=O)Bu\text{-}t]^+[BF_4]^-$ easily transferred its alkyl moiety to a sulfinate anion to form the corresponding alkyl phenyl sulfone and diphenyl telluride, while the base-promoted reaction of $[Ph_2TeCH_2C(=O)Ph]^+[BF_4]^-$ with benzaldehyde afforded a chalcone and diphenyl telluroxide.

Introduction

Telluronium salts are of interest as potential precursors to telluronium ylides and telluranes,[1] which have recently been receiving attention as a new class of reagents for synthesizing olefins,[2] epoxides,[2d,3] cyclopropanes,[4] and alcohols[3f,5] from carbonyl compounds. Telluronium salts such as alkyl-, allyl-, benzyl-, and propargyltelluronium halides are usually prepared by treating a dialkyl telluride with the corresponding halogenoalkanes.[1−5] However, this procedure fails for the general synthesis of alkenyl-, alkynyl-, and aryltelluronium salts due to the low electrophilicity of counterpart reagents, i.e., halogenoalkenes, -alkynes, and -arenes.[6] On the other hand, hypervalent tellurium compounds of the type Ar_2TeX_2 (X denotes a halogen atom or different anionic grouping) are known to possess an electrophilic tellurium center which could react with a carbon nucleophile to generate a new Te−C bond.[1] Lederer in 1920 reported that the reaction of diphenyltellurinyl dichloride with an excess of aryl Grignard reagents gave unsymmetrical triaryltelluronium salts in 10−77% yields.[7] However, his pioneering work has apparently received little attention. This approach seems quite attractive for preparing unsymmetrical telluronium salts, since a variety of organometallic nucleophiles are readily available today. Herein, we report a new general method for the synthesis of 2-oxoalkyl-, 3-oxoalkyl-, allyl-, benzyl-, alkenyl-, and alkynyldiaryltelluronium salts as well as unsymmetrically triarylated telluronium salts through the $BF_3{\cdot}OEt_2$-promoted reaction of diaryltellurinyl difluorides with organosilanes and -stannanes. The present methodology covers the incorporation of $Te{-}C_{sp^3}$, $Te{-}C_{sp^2}$,

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† E-mail: suzuki@kuchem.kyoto-u.ac.jp.

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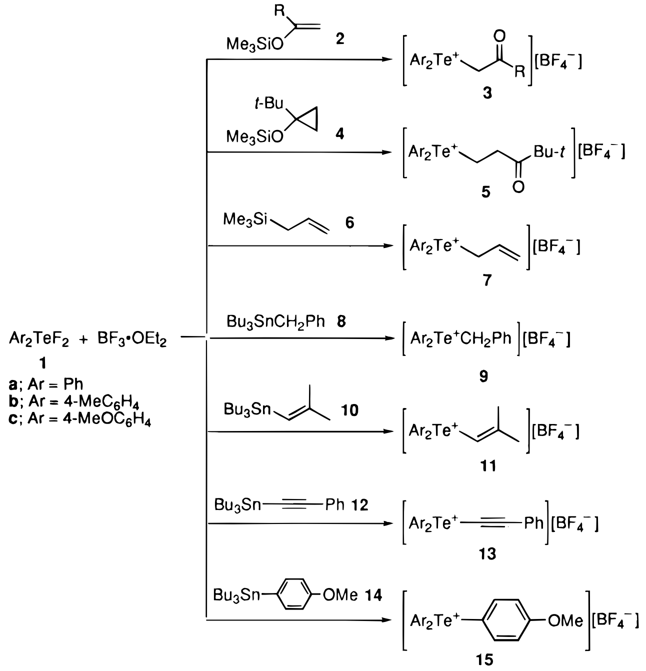
Table 1. Synthesis of Telluronium Salts[a]

run no.	difluoride	silane or stannane	reacn time/h	salt	yield/%
1	Ph_2TeF_2 (**1a**)	t-Bu(Me_3SiO)C=CH_2 (**2a**)	12	**3a** (Ar = Ph, R = t-Bu)	>99
2	**1a**	i-Pr(Me_3SiO)C=CH_2 (**2b**)	12	**3b** (Ar = Ph, R = i-Pr)	>99
3	**1a**	Ph(Me_3SiO)C=CH_2 (**2c**)	12	**3c** (Ar = Ph, R = Ph)	>99
4	p-Tol_2TeF_2 (**1b**)	**2a**	12	**3d** (Ar = p-Tol, R = t-Bu)	>99
5	**1b**	**2c**	12	**3e** (Ar = p-Tol, R = Ph)	>99
6	p-Ans_2TeF_2 (**1c**)	**2c**	12	**3f** (Ar = p-Ans, R = Ph)	>99
7	**1a**	t-Bu(Me_3SiO)CCH_2CH_2 (**4**)	6	**5** (Ar = Ph)	85
8[b]	**1a**	$Me_3SiCH_2CH=CH_2$ (**6**)	3	**7** (Ar = Ph)	>99
9	**1a**	n-Bu_3SnCH_2Ph (**8**)	6	**9a** (Ar = Ph)	89
10	**1c**	**8**	6	**9b** (Ar = p-Ans)	88
11	**1a**	n-$Bu_3SnCH=CMe_2$ (**10**)	4	**11** (Ar = Ph)	87
12	**1a**	n-$Bu_3SnC \equiv CPh$ (**12**)	6	**13a** (Ar = Ph)	96
13	**1c**	**12**	6	**13b** (Ar = p-Ans)	94
14	**1a**	n-Bu_3SnAns-p (**14**)	24	**15** (Ar = Ph)	95

[a] All reactions except for run 8 were carried out in CH_2Cl_2 at room temperature. Legend: p-Tol = p-tolyl; p-Ans = p-anisyl. [b] Reaction was carried out at −50 °C.

and Te−C_{sp} bonds into telluronium salts using easily accessible organotellurium(IV) compounds as substrates. Spectral properties and some reactions of newly obtained telluronium salts, together with a crystal structure analysis, are also presented.

Scheme 1



Results and Discussion

Treatment of diaryltellurinyl difluorides (**1**) with silyl enol ethers (**2**) in the presence of $BF_3 \cdot OEt_2$ in CH_2Cl_2 at room temperature readily gave (2-oxoalkyl)diaryltelluronium tetrafluoroborates (**3**) in quantitative yield (Scheme 1). In this reaction, the Lewis acid plays two important roles; it initially coordinates to **1** to enhance the electrophilicity of the tellurium atom and is subsequently transformed into the counterion for the resulting onium salts **3**. In the absence of the Lewis acid, no reaction took place between **1** and **2** under the same reaction conditions. Since the sole byproduct was volatile fluorotrimethylsilane, analytically pure salts **3** were obtained by simple evaporation of the reaction mixture under reduced pressure. Other alkyltelluronium salts were similarly obtained by an appropriate choice of nucleophiles; 3-oxoalkyl-, allyl-, and benzyldiaryltelluronium tetrafluoroborates (**5**, **7**, and **9**) were prepared by treating **1** with siloxycyclopropane (**4**), allylsilane (**6**), or benzylstannane (**8**), respectively. The major advantages of the present methodology are (1) all reagents are readily accessible, (2) the reaction proceeds under mild conditions, and (3) products are easily isolated in a high state of purity by simple evaporation and/or recrystallization. Noteworthy is that the same procedure can be extended to the synthesis of unsymmetrical alkenyl-, alkynyl-, and aryltelluronium salts (**11**, **13**, and **15**) by using the corresponding organotin reagents (**10**, **12**, and **14**). As mentioned in the Introduction, these types of telluronium salts are difficult to obtain by ordinary approaches. Thus, the present methodology opens a new, convenient route to telluronium salts that are usually inaccessible by nucleophilic reaction of diorganyl tellurides with organic halides. All isolated telluronium salts are thermally stable and stable to hydrolysis by atmospheric moisture. Selected spectral data of several telluronium salts obtained are summarized in Table 2. In the ^1H NMR spectra, the α-protons of **3**, **7**, and **9** were observed at relatively lower field, probably due to the electron-withdrawing effect of the telluronium center. A diagnostic feature in the ^{13}C NMR spectra is the appearance at low field of the alkenyl and alkynyl β-carbon resonances of **11** and **13** as compared to those of the α-carbons. This shows that part of the positive charge on the tellurium center is delocalized through the π-orbitals of the unsaturated carbons. In general, the ^{125}Te NMR spectra of organotellurium compounds provide useful information on the character of the tellurium atom. A recent ^{125}Te NMR study by Huang and co-workers revealed that unsymmetrical alkyldibutyltelluronium salts such as $[Bu_2TeR]^+X^-$, $[Bu_2TeCH_2Ph]^+X^-$, $[Bu_2TeCH_2CH=CH_2]^+X^-$, $[Bu_2TeCH_2CO_2R]^+X^-$, $[Bu_2TeCH_2CN]^+X^-$, and $[Bu_2TeCH_2CONHR]^+X^-$ (Bu denotes i-Bu or n-Bu and X is halogen or tetraphenylborate) show ^{125}Te signals in the range between δ 281 and 602 ppm, depending on the mode of the coordination of the ligands and counteranions.[8] As shown in Table 2, the ^{125}Te chemical shifts of the telluronium salts span the range δ 645−755 ppm. The appearance of ^{125}Te resonances at relatively low

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[8] Zhou, Z. L.; Huang, Y. Z.; Tang, Y.; Chen, Z. H.; Shi, L. P.; Jin, X. L.; Yang, Q. C. *Organometallics* **1994**, *13*, 1575. They observed the ^{125}Te peak of $[Ph_2TeMe]^+[BPh_4]^-$ at 675 ppm.

Table 2. Spectral Data for Selected Telluronium Salts

salt	^{1}H and ^{13}C NMR^a (δ/ppm)	^{125}Te NMR^b (δ/ppm)	IR^c (ν/cm^{-1})	FABMS^d (m/z)
$[Ph_2TeCH_2C({=}O)Bu\text{-}t]^+[BF_4]^-$ (**3a**)	5.16 (α-H); 210.8 (C=O)	683	1678 (C=O)	383
$[Ph_2Te(CH_2)_2C({=}O)Bu\text{-}t]^+[BF_4]^-$ (**5**)	219.3 (C=O)	740	1667 (C=O)	397
$[Ph_2TeCH_2CH{=}CH_2]^+[BF_4]^-$ (**7**)	4.29 (α-H); 119.6 (α-C)	717		325
$[Ph_2TeCH_2Ph]^+[BF_4]^-$ (**9a**)	4.88 (α-H); 39.1 (α-C)	755		375
$[Ph_2TeCH{=}CMe_2]^+[BF_4]^-$ (**11**)	106.8 (α-C), 163.1 (β-C)	645		339
$[Ph_2TeC{\equiv}CPh]^+[BF_4]^-$ (**13a**)	62.5 (α-C), 115.5 (β-C)	736	2153 (C≡C)	385
$[Ph_2TeAns\text{-}p]^+[BF_4]^-$ (**15**)		753		391

[a] Measured in $CDCl_3$ (δ vs TMS). α- and β-C refer to the α- and β-carbon atoms of alkyl, alkenyl, or alkynyl chains. [b] Measured in $CDCl_3$ (δ vs Me_2Te). [c] Measured as a KBr pellet. Absorption of BF_4^- was observed at 1150−900 cm^{-1} for all salts. [d] Measured in 3-nitrobenzyl alcohol. Listed are the $M^+ - BF_4$ fragments due to the most abundant isotope, ^{130}Te.

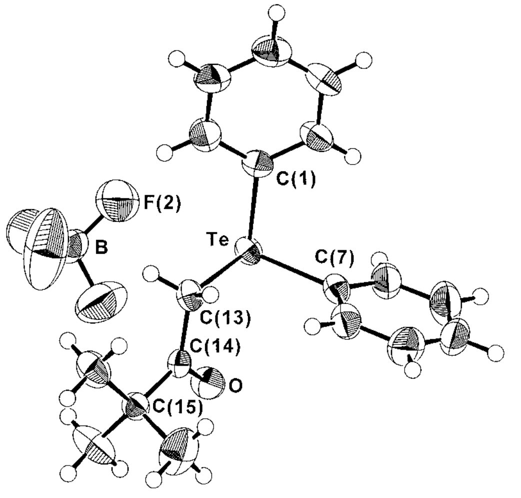

Figure 1. ORTEP drawing of compound **3a** with the atom-numbering scheme.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of Compound 3a, with Estimated Standard Deviations in Parentheses

Bond Lengths			
Te−C(1)	2.129(5)	C(14)−C(15)	1.518(7)
Te−C(7)	2.108(6)	C(14)−O	1.225(7)
Te−C(13)	2.129(6)	Te···F(2)	3.065(5)
C(13)−C(14)	1.497(8)	Te···O	2.892(4)
Bond Angles			
C(1)−Te−C(7)	96.2(2)	C(13)−C(14)−C(15)	119.7(5)
C(1)−Te−C(13)	94.8(2)	C(13)−C(14)−O	118.9(5)
C(7)−Te−C(13)	98.9(2)	C(15)−C(14)−O	121.4(5)
Te−C(13)−C(14)	107.4(4)		

field may be attributed to the combined electronic effect of the phenyl rings and the counterion BF_4^-. Ligands other than the phenyl group may also exert considerable influence on the ^{125}Te chemical shifts. Most characteristic is the alkenyltelluronium salt **11**, which showed the ^{125}Te resonance at highest field among all the telluronium salts examined. Perhaps the electron delocalization from the vinylic π-orbital to the cationic tellurium center is responsible for the upfield shift of the ^{125}Te resonance of **11**. In the IR spectra, a broad absorption due to the fluoroborate anion was observed at around 1150−950 cm^{-1} for all the salts. FAB-MS spectra showed a $M^+ - BF_4$ fragment as the stable ion peak. All these spectral features are in accord with the onium nature of the present compounds.

The onium structure was further confirmed for **3a** by X-ray crystal analysis. The molecular structure of **3a** is shown in Figure 1, together with the atom-numbering system. The bond lengths and angles are given in Table 3. Because of the D_2 crystal point group and $Z = 4$, the chirality has been examined by the test of the R factor ratio.[9] The R_w factor for the structure refinement without anomalous dispersion effects was 0.0317 for 227 variables and 1924 observations. Inclusion of the anomalous dispersion gave the R_w factors of 0.0353 and 0.0406 for the present species and its enantiomeric structure, respectively, which yielded an R factor ratio of 1.15. The corresponding significant point is $R_{b,N,\alpha} = R_{1,1697,0.005} = 1.002$, so that the enantiomeric structure can be rejected with a probability higher than 99.5%.[10] As shown in Figure 1 and Table 3, this molecule possesses an ion-pair form with the tricoordinated telluronium center having a distorted-pyramidal geometry. The tetrafluoroborate anion is spatially apart (Te···F = 3.065(5) Å) and therefore appears to have only a weak electrostatic interaction with the tellurium center. The observed Te−C bond lengths (2.108(6)−2.129(6) Å) are close to the reported values: $[Me_3Te]^+[BPh_4]^-$ (2.113(14)−2.162(7) Å),[11] $[Me_3Te]^+I^-$ (2.114(10)−2.138(10) Å),[8] $[i\text{-}Bu_2TePh]^+Br^-$ (2.113(14)−2.122(14) Å),[8] and $[Ph_2TeMe]^+[BPh_4]^-$ (2.122(6)−2.131(6) Å).[8] Noteworthy is the intramolecular distance between the tellurium and oxygen atoms (2.892(4) Å), which is longer than the sum of their covalent radii (2.02 Å) but shorter than that of their van der Waals radii (3.56 Å).[12] This may arise from a weak nonbonding interaction between the tellurium and oxygen atoms.[13] A lower shift of the IR absorption due to the C=O stretching (1678 cm^{-1}) of **3a** as compared to that of pinacolone (1709 cm^{-1}) supports this interpretation. Somewhat larger C−Te−C bond angles (94.8(2)−98.9(2)°) as compared to those of $[Me_3Te]^+[BPh_4]^-$ (90.4(5)−93.0(4)°), $[Me_3Te]^+I^-$ (92.1(4)−95.4(4)°), $[i\text{-}Bu_2TePh]^+Br^-$ (92.8(6)−93.7(5)°), and $[Ph_2TeMe]^+[BPh_4]^-$ (91.5(2)−97.7(2)°) may partially be attributed to this type of coordinative interaction.[14]

To obtain some information on the reactivity of these telluronium salts, reactions with a nucleophile and a base were investigated. Reaction of $[Ph_2TeCH_2CH_2C({=}O)Bu\text{-}t]^+[BF_4]^-$ (**5**) with sodium benzenesulfinate in DMF gave the alkyl phenyl sulfone $PhSO_2CH_2CH_2C({=}O)Bu\text{-}t$ in good yield along with quantitative recovery of diphenyl telluride, while **3** and **11** failed to transfer their organyl ligands to the sulfinate. The last two

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(10) *International Tables for X-Ray Crystallography*; Kluwer Academic: Dordrecht, The Netherlands, 1989; Vol. 4, p 288.

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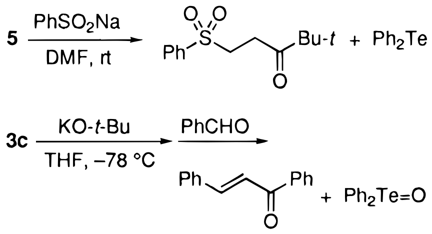
(12) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(13) If we consider a possible coordination by fluorine and carbonyl oxygen atoms, the tellurium atom of **3a** should be regarded as five-coordinate with a distorted-square-pyramidal geometry.

(14) The C−Te−C angles of Ph_3TeX, where X denotes a ligand such as NCO, NCS, S_2PPh_2, $(SPPh_2)_2N$, S_2COR, or S_2COR, are relatively wide open. See: (a) Titus, D. D.; Lee, J.-S.; Ziolo, R. F. *J. Organomet. Chem.* **1976**, *120*, 381. (b) Lee, J.-S.; Titus, D. D.; Ziolo, R. F. *Inorg. Chem.* **1977**, *16*, 2487. (c) Silvestru, A.; Haiduc, I.; Toscano, R. A.; Breunig, H. J. *Polyhedron* **1995**, *14*, 2047. (d) Singh, A. K.; Basumatary, J. K.; Singh, T. P.; Padmanabhan, B. *J. Organomet. Chem.* **1992**, *424*, 33.

Scheme 2



compounds stand in contrast to the iodonium [PhI-CH=CRR′]$^+$[BF$_4$]$^-$[15] and bismuthonium salts [Ph$_3$BiCH$_2$(C=O)R]$^+$[BF$_4$]$^-$[16] and [Ph$_3$BiCH=CRR′]$^+$[BF$_4$]$^-$,[17] which readily transfer their organyl ligands to the sulfinate. As can be judged from these observations, the leaving ability of the diphenyltelluronio group apparently is lower than those of the phenyliodonio and triphenylbismuthonio groups. A similar trend also was observed in the base-promoted coupling reaction of [Ar$_2$TeCH$_2$C(=O)R]$^+$[BF$_4$]$^-$ with aldehyde; treatment of [Ph$_2$TeCH$_2$C(=O)Ph]$^+$[BF$_4$]$^-$ (**3c**) with KO-*t*-Bu followed by addition of benzaldehyde gave the chalcone PhCH=CHC(=O)Ph in quantitative yield, together with white polymeric diphenyl telluroxide. A similar reaction of phenacyltriphenylbismuthonium tetrafluoroborate produced 1,3-diphenyl-2,3-epoxypropan-1-one and triphenylbismuthane in good yields.[18] This difference in the mode of reactivity may be due to the greater affinity of the carbonyl oxygen atom of the aldehyde toward the telluronio moiety than toward the bismuthonio moiety in the transition state of the condensation reaction.

Experimental Section

General Comments. Melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{125}Te NMR spectra were recorded on Varian Gemini-200 (^{1}H and ^{13}C) and JEOL α-500 (^{125}Te) spectrometers in CDCl$_3$. Chemical shifts were based on internal tetramethylsilane (^{1}H and ^{13}C) and external neat dimethyl telluride (^{125}Te). IR spectra were observed on a Shimadzu FTIR-8100S spectrophotometer. EI mass spectra were measured at 70 eV on a Shimadzu GCMS-QP2000A spectrometer. FAB mass spectra were recorded on a JEOL JMS-HS110 spectrometer using 3-nitrobenzyl alcohol as a matrix. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University. Difluorides **1** were prepared from Ar$_2$TeCl$_2$[19,20] according to the reported procedure.[21] All reactions were carried out under an Ar atmosphere. CH$_2$Cl$_2$ and THF were distilled from CaH$_2$ and sodium benzophenone ketyl, respectively, before use. Column chromatography was performed on silica gel (Wakogel, 200 mesh).

(2-Oxoalkyl)diaryltelluronium Tetrafluoroborate (3). Typical Procedure. To a stirred solution of **1a** (320 mg, 1 mmol) in CH$_2$Cl$_2$ (5 mL) was added at 0 °C BF$_3$·OEt$_2$ (0.12 mL, 1 mmol). After 1 h, **2a** (172 mg, 1 mmol) was introduced and the resulting mixture was stirred for an additional 12 h at room temperature to complete the reaction. Evaporation of the solvent under reduced pressure left a crystalline residue, which was recrystallized from Et$_2$O−CH$_2$Cl$_2$ (10:1) to afford **3a** (468 mg, 100%) as colorless crystals.

(3,3-Dimethyl-2-oxobutyl)diphenyltelluronium tetrafluoroborate (3a): mp 176−178 °C; ^{1}H NMR δ 1.22 (s, 9H, *t*-Bu), 5.16 (s, 2H, CH$_2$), 7.50−7.68 (m, 10H, Ar H); ^{13}C NMR δ 26.6, 44.8, 48.5, 120.0, 131.1, 132.7, 134.5, 210.8; ^{125}Te NMR δ 683; FABMS *m/z* 383 (M$^+$ − BF$_4$, ^{130}Te), 381 (M$^+$ − BF$_4$, ^{128}Te), 379 (M$^+$ − BF$_4$, ^{126}Te), 284, 282, 280; IR (KBr) ν_{max} 1678 (C=O), 1150−1000 (BF$_4^-$) cm^{-1}. Anal. Calcd for C$_{18}$H$_{21}$BF$_4$OTe: C, 46.22; H, 4.52. Found: C, 45.89; H, 4.59.

(3-Methyl-2-oxobutyl)diphenyltelluronium tetrafluoroborate (3b): mp 136−137 °C; ^{1}H NMR δ 1.14 (d, J = 7.0 Hz, 6H, Me), 2.90 (sept, J = 7.0 Hz, 1H, CH), 5.01 (s, 2H, CH$_2$), 7.45−7.70 (m, 10H, Ar H); ^{13}C NMR δ 18.0, 40.4, 48.9, 120.0, 131.0, 132.5, 134.6, 209.0; FABMS *m/z* 369 (M$^+$ − BF$_4$, ^{130}Te), 367 (M$^+$ − BF$_4$, ^{128}Te), 365 (M$^+$ − BF$_4$, ^{126}Te), 284, 282, 280; IR (KBr) ν_{max} 1696 (C=O), 1150−1000 (BF$_4^-$) cm^{-1}. Anal. Calcd for C$_{17}$H$_{19}$BF$_4$OTe: C, 45.00; H, 4.22. Found: C, 44.83; H, 4.21.

Phenacyldiphenyltelluronium tetrafluoroborate (3c): mp 196−197 °C; ^{1}H NMR δ 5.57 (s, 2H, CH$_2$), 7.42−7.74 (m, 13H, Ar H), 7.98−8.05 (m, 2H, Ar H); ^{125}Te NMR δ 679; FABMS *m/z* 403 (M$^+$ − BF$_4$, ^{130}Te), 401 (M$^+$ − BF$_4$, ^{128}Te), 399 (M$^+$ − BF$_4$, ^{126}Te), 284, 282, 280; IR (KBr) ν_{max} 1663 (C=O), 1150−950 (BF$_4^-$) cm^{-1}. Anal. Calcd for C$_{20}$H$_{17}$BF$_4$OTe: C, 49.25; H, 3.51. Found: C, 49.29; H, 3.50.

(3,3-Dimethyl-2-oxobutyl)bis(4-methylphenyl)telluronium tetrafluoroborate (3d): mp 81−83 °C; ^{1}H NMR δ 1.19 (s, 9H, *t*-Bu), 2.40 (s, 6H, Me), 5.07 (s, 2H, CH$_2$), 7.32 (d, J = 8.1 Hz, 4H, Ar H), 7.51 (d, J = 8.1 Hz, 4H, Ar H); ^{13}C NMR δ 21.5, 26.5, 44.6, 48.4, 115.9, 131.8, 134.3, 143.5, 210.9; FABMS *m/z* 411 (M$^+$ − BF$_4$, ^{130}Te), 409 (M$^+$ − BF$_4$, ^{128}Te), 407 (M$^+$ − BF$_4$, ^{126}Te), 312, 310, 308; IR (KBr) ν_{max} 1686 (C=O), 1150−950 (BF$_4^-$) cm^{-1}. Anal. Calcd for C$_{20}$H$_{25}$BF$_4$OTe: C, 48.45; H, 5.08. Found: C, 48.72; H, 5.22.

Bis(4-methylphenyl)phenacyltelluronium tetrafluoroborate (3e): mp 185−187 °C; ^{1}H NMR δ 2.38 (s, 6H, Me), 5.46 (s, 2H, CH$_2$), 7.30 (d, J = 8.2 Hz, 4H, Ar H), 7.44 (t, J = 7.9 Hz, 2H, Ar H), 7.54−7.63 (m, 5H, Ar H), 7.98 (d, J = 7.9 Hz, 2H, Ar H); ^{13}C NMR δ 21.5, 48.3, 116.2, 129.0, 129.7, 131.8, 133.6, 134.5, 135.1, 143.4, 193.8; FABMS *m/z* 431 (M$^+$ − BF$_4$, ^{130}Te), 429 (M$^+$ − BF$_4$, ^{128}Te), 427 (M$^+$ − BF$_4$, ^{126}Te), 312, 310, 308; IR (KBr) ν_{max} 1653 (C=O), 1150−950 (BF$_4^-$) cm^{-1}. Anal. Calcd for C$_{22}$H$_{21}$BF$_4$OTe: C, 51.23; H, 4.10. Found: C, 50.83; H, 4.04.

Bis(4-methoxyphenyl)phenacyltelluronium tetrafluoroborate (3f): mp 76−78 °C; ^{1}H NMR δ 3.73 (s, 6H, Me), 5.40 (s, 2H, CH$_2$), 6.94 (d, J = 8.8 Hz, 4H, Ar H), 7.36 (t, J = 7.4 Hz, 2H, Ar H), 7.54 (t, J = 7.4 Hz, 1H, Ar H), 7.64 (d, J = 8.8 Hz, 4H, Ar H), 7.92 (d, J = 7.5 Hz, 2H, Ar H); ^{13}C NMR δ 47.6, 55.5, 109.1, 116.8, 129.0, 129.7, 133.5, 135.1, 136.1, 162.8, 194.3; FABMS *m/z* 463 (M$^+$ − BF$_4$, ^{130}Te), 461 (M$^+$ − BF$_4$, ^{128}Te), 459 (M$^+$ − BF$_4$, ^{126}Te), 344, 342, 340; IR (KBr) ν_{max} 1655 (C=O), 1150−950 (BF$_4^-$) cm^{-1}. Anal. Calcd for C$_{22}$H$_{21}$BF$_4$O$_3$Te: C, 48.24; H, 3.86. Found: C, 48.30; H, 3.74.

(4,4-Dimethyl-3-oxopentyl)diphenyltelluronium Tetrafluoroborate (5). To a stirred solution of **1a** (320 mg, 1 mmol) in CH$_2$Cl$_2$ (5 mL) was added BF$_3$·OEt$_2$ (0.12 mL, 1 mmol) at 0 °C. After 1 h, 1-(1,1-dimethylethyl)-1-(trimethylsiloxy)cyclopropane (**4**; 186 mg, 1 mmol) was introduced and the resulting mixture was stirred for an additional 6 h at room temperature to complete the reaction. Evaporation of the solvent under reduced pressure left an oily residue, which was crystallized from Et$_2$O−CH$_2$Cl$_2$ (5:1) to afford **5** (410 mg, 85%) as crystals: mp 126−128 °C; ^{1}H NMR δ 1.14 (s, 9H, *t*-Bu), 3.42 (t, J = 6.0 Hz, 2H, CH$_2$), 3.56 (t, J = 6.0 Hz, 2H, CH$_2$), 7.40−7.70 (m, 10H, Ar H); ^{13}C NMR δ 26.2, 27.2, 32.0, 44.1, 123.9, 130.7, 132.1, 134.1, 219.3; ^{125}Te NMR δ 740; FABMS *m/z* 397 (M$^+$ − BF$_4$, ^{130}Te), 395 (M$^+$ − BF$_4$, ^{128}Te), 393 (M$^+$ − BF$_4$, ^{126}Te), 284, 282, 280, 207, 205, 203; IR (KBr) ν_{max} 1667

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(C=O), 1150−950 (BF_4^-) cm^{-1}. Anal. Calcd for $C_{19}H_{23}BF_4OTe$: C, 47.37; H, 4.81. Found: C, 47.36; H, 4.76.

Allyldiphenyltelluronium Tetrafluoroborate (7). To a stirred solution of **1a** (320 mg, 1 mmol) in CH_2Cl_2 (5 mL) was added $BF_3{\cdot}OEt_2$ (0.12 mL, 1 mmol) at 0 °C. After 1 h, allyltrimethylsilane **6** (0.16 mL, 1 mmol) was introduced at −50 °C and the resulting mixture was warmed to room temperature over 3 h. Evaporation of the solvent under reduced pressure gave **7** (410 mg, 100%) as a glass: ^{1}H NMR δ 4.29 (d, J = 8.1 Hz, 2H, CH_2), 5.10−5.24 (m, 2H, CH=C*H*$_2$), 5.65−5.92 (m, 1H, C*H*=CH_2), 7.45−7.70 (m, 10H, Ar H); ^{13}C NMR δ 119.6, 124.9, 126.5, 130.2, 131.0, 132.6, 134.5; ^{125}Te NMR δ 717; FABMS m/z 325 ($M^+ - BF_4$, ^{130}Te), 323 ($M^+ - BF_4$, ^{128}Te), 321 ($M^+ - BF_4$, ^{126}Te), 284, 282, 280, 207, 205, 203; IR (neat) ν_{max} 1200−950 (BF_4^-) cm^{-1}. Although spectroscopic data clearly supported a high state of purity of **7**, we were not successful in obtaining satisfactory analytical data of an accuracy within ±0.4%.

Benzyldiaryltelluronium Tetrafluoroborate (9). Typical Procedure. To a stirred solution of **1a** (320 mg, 1 mmol) in CH_2Cl_2 (5 mL) was added $BF_3{\cdot}OEt_2$ (0.12 mL, 1 mmol) at 0 °C. After 1 h benzyltributylstannane (**8**; 381 mg, 1 mmol) was introduced and the resulting mixture was stirred for an additional 24 h at room temperature to complete the reaction. Evaporation of the solvent under reduced pressure left an oily residue, which was crystallized from $Et_2O-CH_2Cl_2$ (5:1) to afford **9a** (410 mg, 89%) as crystals.

Benzyldiphenyltelluronium tetrafluoroborate (9a): mp 129−131 °C; ^{1}H NMR δ 4.88 (s, 2H, CH_2), 6.95−7.20 (m, 5H, Ar H), 7.40−7.60 (m, 10H, Ar H); ^{13}C NMR δ 39.1, 120.7, 128.8, 128.9, 130.0, 130.2, 130.8, 132.5, 134.7; ^{125}Te NMR δ 755; FABMS m/z 375 ($M^+ - BF_4$, ^{130}Te), 373 ($M^+ - BF_4$, ^{128}Te), 371 ($M^+ - BF_4$, ^{126}Te), 284, 282, 280, 207, 205, 203; IR (neat) ν_{max} 1150−950 (BF_4^-) cm^{-1}. Anal. Calcd for $C_{19}H_{17}BF_4Te$: C, 49.64; H, 3.73. Found: C, 49.36; H, 3.71.

Benzylbis(4-methoxyphenyl)telluronium tetrafluoroborate (9b): glass; ^{1}H NMR δ 3.80 (s, 6H, Me), 4.78 (s, 2H, CH_2), 6.90−7.20 (m, 9H, Ar H), 7.36 (d, J = 8.4 Hz, 4H, Ar H); ^{13}C NMR δ 38.9, 55.5, 109.7, 116.6, 128.7, 128.9, 130.2, 130.3, 136.2, 162.9; FABMS m/z 435 ($M^+ - BF_4$, ^{130}Te), 433 ($M^+ - BF_4$, ^{128}Te), 431 ($M^+ - BF_4$, ^{126}Te), 344, 342, 340, 237, 235, 233; IR (KBr) ν_{max} 1150−950 (BF_4^-) cm^{-1}. Anal. Calcd for $C_{21}H_{21}BF_4O_2Te$: C, 48.52; H, 4.07. Found: C, 48.06; H, 4.20.

(2-Methyl-1-propenyl)diphenyltelluronium Tetrafluoroborate (11). To a stirred solution of **1a** (320 mg, 1 mmol) in CH_2Cl_2 (5 mL) was added $BF_3{\cdot}OEt_2$ (0.12 mL, 1 mmol) at 0 °C. After 1 h, (2-methyl-1-propenyl)tributylstannane (**10**; 345 mg, 1 mmol) was added and the resulting mixture was stirred for an additional 24 h at room temperature to complete the reaction. Evaporation of the solvent under reduced pressure left an oily residue, which was crystallized from $Et_2O-CH_2Cl_2$ (5:1) to afford **11** (369 mg, 87%) as crystals: mp 92−93 °C; ^{1}H NMR δ 2.17 (s, 3H, Me), 2.19 (s, 3H, Me), 6.29 (s, 1H, CH), 7.45−7.75 (m, 10H, Ar H); ^{13}C NMR δ 26.3, 27.2, 106.8, 121.8, 131.2, 132.6, 133.9, 163.1; ^{125}Te NMR δ 645; FABMS m/z 339 ($M^+ - BF_4$, ^{130}Te), 337 ($M^+ - BF_4$, ^{128}Te), 335 ($M^+ - BF_4$, ^{126}Te), 284, 282, 280, 262, 260, 258, 207, 205, 203; IR (KBr) ν_{max} 1150−950 (BF_4^-) cm^{-1}. Anal. Calcd for $C_{16}H_{17}BF_4Te$: C, 45.35; H, 4.04. Found: C, 44.95; H, 4.02.

Diaryl(phenylethynyl)telluronium Tetrafluoroborate (13). Typical Procedure. To a stirred solution of **1a** (320 mg, 1 mmol) in CH_2Cl_2 (5 mL) was added $BF_3{\cdot}OEt_2$ (0.12 mL, 1 mmol) at 0 °C. After 1 h, (phenylethynyl)tributylstannane (**12**; 392 mg, 1 mmol) was added and the resulting mixture was stirred for an additional 6 h at room temperature to complete the reaction. Evaporation of the solvent under reduced pressure left an oily residue, which was crystallized from $Et_2O-CH_2Cl_2$ (5:1) to afford **13a** (451 mg, 96%) as crystals.

Diphenyl(phenylethynyl)telluronium tetrafluoroborate (13a): mp 132−134 °C; ^{1}H NMR δ 7.4−7.7 (m, 11H, Ar H), 8.0 (m, 4H, Ar H); ^{13}C NMR δ 62.5, 115.5, 119.3, 125.3, 128.8, 131.1, 131.5, 132.7, 133.0, 133.9; ^{125}Te NMR δ 736; FABMS m/z 385 ($M^+ - BF_4$, ^{130}Te), 383 ($M^+ - BF_4$, ^{128}Te), 381 ($M^+ - BF_4$, ^{126}Te), 284, 282, 280, 207, 205, 203; IR (KBr) ν_{max} 2153 (C≡C), 1200−900 (BF_4^-) cm^{-1}. Anal. Calcd for $C_{20}H_{15}BF_4Te$: C, 51.14; H, 3.22. Found: C, 51.05; H, 3.31.

Bis(4-methoxyphenyl)(phenylethynyl)telluronium tetrafluoroborate (13b): mp 143−145 °C; ^{1}H NMR δ 3.81 (s, 6H, Me), 7.03 (d, J = 9.1 Hz, 4H, Ar H), 7.30−7.64 (m, 5H, Ar H), 7.89 (d, J = 9.1 Hz, 4H, Ar H); ^{13}C NMR δ 55.6, 62.4, 114.5, 115.7, 116.8, 119.4, 128.8, 131.4, 132.9, 135.6, 163.1; FABMS m/z 445 ($M^+ - BF_4$, ^{130}Te), 443 ($M^+ - BF_4$, ^{128}Te), 441 ($M^+ - BF_4$, ^{126}Te), 344, 342, 340, 237, 235, 233; IR (KBr) ν_{max} 2164 (C≡C), 1150−950 (BF_4^-) cm^{-1}. Anal. Calcd for $C_{22}H_{19}BF_4O_2Te$: C, 49.88; H, 3.61. Found: C, 49.44; H, 3.78.

(4-Methoxyphenyl)diphenyltelluronium Tetrafluoroborate (15). To a stirred solution of **1a** (320 mg, 1 mmol) in CH_2Cl_2 (5 mL) was added $BF_3{\cdot}OEt_2$ (0.12 mL, 1 mmol) at 0 °C. After 1 h, (4-methoxyphenyl)tributylstannane (**14**; 400 mg, 1 mmol) was added and the resulting mixture was stirred for an additional 24 h at room temperature. Evaporation of the solvent under reduced pressure left a glassy residue, which was thoroughly washed with hexane and $Et_2O-CH_2Cl_2$ (10:1) successively to afford pure **15** (450 mg, 95%) as a glass: ^{1}H NMR δ 3.84 (s, 3H, Me), 7.05 (d, J = 8.4 Hz, 2H, Ar H), 7.40−7.70 (m, 12H, Ar H); ^{13}C NMR δ 55.7, 110.6, 117.1, 122.0, 131.2, 132.8, 134.3, 136.3, 163.3; ^{125}Te NMR δ 753; FABMS m/z 391 ($M^+ - BF_4$, ^{130}Te), 389 ($M^+ - BF_4$, ^{128}Te), 387 ($M^+ - BF_4$, ^{126}Te), 314, 312, 310, 284, 282, 280; IR (KBr) ν_{max} 1150−950 (BF_4^-) cm^{-1}. Anal. Calcd for $C_{19}H_{17}BF_4OTe$: C, 47.97; H, 3.60. Found: C, 47.81; H, 3.64.

Reaction of 5 with Sodium Sulfinate. A mixture of **5** (96 mg, 0.2 mmol), sodium benzenesulfinate dihydrate (200 mg, 1.0 mmol), and DMF (2 mL) was stirred at room temperature. After 2 h, the reaction mixture was diluted with Et_2O (5 mL) and water (5 mL) and the organic phase was extracted with Et_2O (5 mL × 2). The combined extracts were washed with H_2O (5 mL × 2), dried ($MgSO_4$), and concentrated under reduced pressure to leave an oily residue, which was chromatographed on silica gel to afford diphenyl telluride (55 mg, 98%) and 1-(phenylsulfonyl)-4,4-dimethylpentan-3-one (48 mg, 94%): ^{1}H NMR δ 1.14 (s, 9H, *t*-Bu), 3.02 (t, J = 7.9 Hz, 2H, CH_2), 3.37 (t, J = 7.9 Hz, 2H, CH_2), 7.52−7.70 (m, 3H, Ar H), 7.88−7.94 (m, 2H, Ar H); EIMS m/z 197 ($M^+ - 57$), 142, 125, 77, 57; IR (KBr) ν_{max} 1709 (C=O), 1308 (SO_2), 1152 (SO_2).

Reaction of 3c with Benzaldehyde in the Presence of KO-*t*-Bu. To a suspension of **3c** (244 mg, 0.5 mmol) in THF (5 mL) was added KO-*t*-Bu (56 mg, 0.5 mmol) at −78 °C. After 10 min, benzaldehyde (53 mg, 0.5 mmol) was added and the mixture was warmed to room temperature. The resulting white suspension was filtered through a Celite bed, and the filtrate was concentrated under reduced pressure to leave an oily residue, which was chromatographed on a short silica gel column to afford chalcone (102 mg, 98%), identical with an authentic specimen.

Crystallographic Data for Compound 3a. A crystal of dimensions 0.180 × 0.250 × 0.330 mm, grown from $Et_2O-CH_2Cl_2$ (2:1) at ambient temperature, was used for X-ray diffraction. $C_{18}H_{21}BF_4OTe$: mw 467.77; orthorhombic; space group $P2_12_12_1$; a = 11.700(1) Å; b = 15.153(3) Å; c = 10.741(3) Å; V = 1904.2(6) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centered reflections in the range $29.06 < 2\theta < 29.99°$, 300 K, Mo Kα radiation, λ = 0.71069 Å); Z = 4; D_c = 1.631 g cm^{-3}; μ(Mo Kα, λ = 0.710 69 Å) = 16.02 cm^{-1}; $F(000)$ = 920. Intensity data were collected on a Rigaku AFC5R diffractometer using graphite-monochromated Mo Kα radiation from a fine focus anode of 12 kW type rotating anode generator with the $\omega-2\theta$ scan technique to a maximum 2θ value of 55.0°. Data were corrected for Lorentz and polarization effects. The intensities of 3 representative reflections, which were measured after every 150 reflections, declined by 1.74%. A linear correction factor was applied to the data to account for this phenomenon. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.86 to 1.00. Scans of $(0.94 + 0.30 \tan \theta)°$ were made at a speed of 16.0° min^{-1} (in ω). The structure was solved by a combination of the Patterson method and direct methods.[22] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1924 observed reflections ($I > 3.00\sigma(I)$) and 227 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.030$ and $R_w = 0.029$. The weighting scheme $w = 1/\sigma^2(F_o)$, was employed. Neutral atom-scattering factors were taken from Cromer and Waber.[23] Anomalous dispersion effects were included in F_c;[24] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[25] All calculations were performed using the TEXSAN[26] crystallographic software package of Molecular Structure Corporation. The ORTEP[27] program was used to obtain Figure 1. Selected bond lengths and bond angles are given in Table 3.

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Supporting Information Available: Tables of experimental details for the X-ray diffraction study, atomic coordinates, thermal parameters, bond distances and angles, torsion angles, intermolecular distances and angles, and least-squares planes and figures giving additional views and unit cell packing for **3a** (25 pages). Ordering information is given on any current masthead page.

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