17-3; $\mathrm{EtC{\equiv}CEt}$, 928-49-4; $\mathrm{PhC{\equiv}CPh}$, 501-65-5; $\mathrm{MeC{\equiv}CBu^t}$, 999-78-0; $\mathrm{Me_3SiC{\equiv}CMe}$, 6224-91-5; $\mathrm{PhC{\equiv}CMe}$, 673-32-5; $\mathrm{PhC{\equiv}CSiMe_3}$, 2170-06-1; $\mathrm{MeO_2CC{\equiv}CMe}$, 23326-27-4; $\mathrm{MeO_2CC{\equiv}CSiMe_3}$, 42201-71-8; 1-*tert*-butyl-3-phenylpyrrole, 20946-89-8.

Supplementary Material Available: For **1c**, **2l**, and **2o** tables of anisotropic thermal parameters, bond lengths and angles, and calculated hydrogen atom positions (12 pages); tables of structure factors (21 pages). Ordering information is given on any current masthead page.

New C–C Bond Formation Reactions Using Bis(acylmethyl)- and Bis[(alkoxycarbonyl)methyl]tellurium Dichlorides

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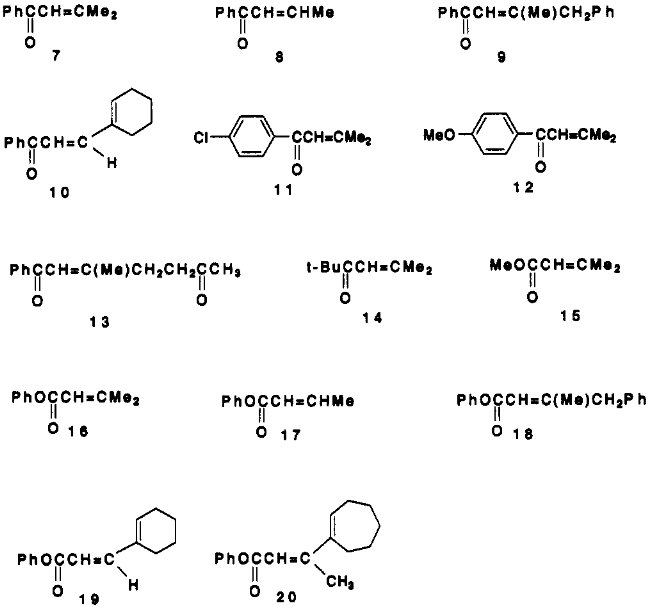
The reaction of organotellurium chlorides with nucleophilic stabilized carbanions has been surveyed. A combination of the bis(organo)tellurium dichlorides [$\mathrm{(R^1COCH_2)_2TeCl_2}$] and lithium nitronates [$\mathrm{LiC(NO_2)R^2R^3}$] led to the coupling products ($\mathrm{R^1COCH{=}CR^2R^3}$) in high to modest yields. This reaction did not involve an S_N2 process nor a radical one with respect to C–C bond formation but was likely to proceed by a polar mechanism that was initiated by coordination of the nitronate oxygen atom to the tellurium followed by intramolecular C–C bond formation and subsequent elimination of nitro and tellurium moieties. To know the exact structure of the starting tellurium compounds, an X-ray analysis of $\mathrm{(PhOCOCH_2)_2TeCl_2}$ was performed, and an intramolecular interaction between the carbonyl oxygen of a $\mathrm{PhOCOCH_2}$ group and the tellurium was not observed.

Introduction

$\mathrm{TeCl_4}$ serves as the Lewis acid[1] and exhibits moderate oxo- and thiophilicity to undergo coordination of the heteroatoms to the tellurium.[2] By using this property, several useful chemical transformations have been devised.[2] Bis(organo)tellurium dichlorides and organotellurium trichlorides are also considered to possess Lewis acidity, due to the inductive effect of the chlorine atoms linked to the tellurium and the general ability of a tellurium atom to take hypervalent bond state.[3] Further, this inductive effect of the chlorine atoms forced the carbon atom of the C–Te bond to positively polarize, in spite of the lower electronegativity of tellurium (2.1) compared with that of carbon (2.55). Thus, we envisioned that this Lewis acidity or oxophilicity and highly polarized nature of organotellurium chlorides must permit them to serve as appropriate electrophiles for nucleophilic substitution reaction, especially for the selective C-alkylation of ambident nucleophiles having O- and C-alkylation sites by blocking O-alkylation owing to an interaction between the oxygen and tellurium atoms. In this context, C-phenylation of phenols, 1,3-dicarbonyl compounds, and other stabilized anions with pentavalent triphenyl- or tetraphenylbismuthonium reagents has been accomplished by Barton and co-workers.[4] To the best of our knowledge, however, there has been no report that organotellurium chlorides, which are now readily available,[3,5,6] could be used as the electrophile for new C–C bond forming reaction.

We have been exploring new bond forming reactions using aliphatic nitro compounds as both the nucleophile and the electrophile.[7] Selective S_N2 type C-alkylation of ambident anions of nitroalkanes is still a remaining problem to be solved.[8] As specific cases, it was found that primary and secondary alkyl cobaloximes[9] and alkylmercury halides[10] and perfluoroiodides[11] underwent C-

Chart I



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† Faculty of General Education, Ehime University.
‡ Faculty of Science, Ehime University.
§ Kyoto University.

(1) (a) Dermer, O. C.; Wilson, D. M.; Johnson, F. M.; Dermer, V. H. *J. Am. Chem. Soc.* **1941**, *63*, 2881. (b) Gunter, W. H. H.; Nepywoda, J.; Chu, J. Y. C. *J. Organomet. Chem.* **1974**, *74*, 79. (c) Bukka, K.; Satchell, R. S. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1110.

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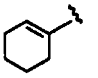
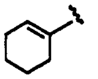
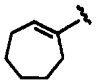
Table I. Reaction of Bis(acylmethyl)- and Bis[(alkoxycarbonyl)methyl]tellurium Dichlorides with Nitronate Anions (eq 1)[a]

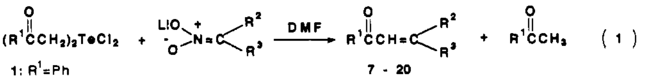
entry	R^1	R^2	R^3	temp (°C)	time (h)	product	yield (%)
1	Ph	Me	Me	25	2	**7**	96(21)[b] (12),[c] (43)[d]
2	Ph	H	Me	25	2	**8**	90
3	Ph	Me	CH_2Ph	25	2	**9**[e]	66
4	Ph	H		25	2	**10**	52
5	4-ClC_6H_5	Me	Me	25	2	**11**	98
6	4-$MeOC_6H_5$	Me	Me	25	2	**12**	70
7	Ph	Me	$CH_2CH_2COCH_3$	25	2	**13**[f]	50
8	*t*-Bu	Me	Me	70	4	**14**	82(4)[g]
9	MeO	Me	Me	60	2	**15**	96(8)[g]
10	PhO	Me	Me	70	2	**16**	71(24)[g]
11	PhO	H	Me	70	12	**17**	22
12	PhO	Me	CH_2Ph	70	12	**18**[h]	51
13	PhO	H		70	12	**19**[i]	30
14	PhO	Me		70	12	**20**[j]	50

[a] All reactions were run under argon atmosphere using 2.0 mmol of the bis(organo)tellurium dichloride and 4.0 mmol of the lithium nitronate in DMF (5 mL). [b] Reaction was performed in THF. [c] Reaction was run in EtOH. [d] One equivalent of $LiCMe_2NO_2$ was used. [e] $E/Z = 1/1$. [f] $E/Z = 2/1$. [g] Recation was performed at 25 °C. [h] $E/Z = 1/1$. [i] $E/Z = 8/3$. [j] $E/Z = 7/3$.

alkylation by nitronate anions under radical conditions. Thus, we focused our attention on using organotellurium chlorides hitherto unexplored with regard to their reaction due to the above reason and surveyed the reaction of various organotellurium chlorides with aliphatic nitonate anions and other stabilized carbanions. As a result, we found that a new coupling reaction occurred between nitronate anions and bis(acylmethyl)-[5] or bis[(alkoxycarbonyl)methyl]tellurium dichlorides (**1**–**6**). In this account, we describe these experimental results and discuss the scope and limitations along with the reaction mechanism.

Results and Discussion

A variety of secondary and tertiary nitronate anions are allowed to react with bis(organo)tellurium dichlorides **1**–**6** in DMF at 25–70 °C to give the corresponding α,β-unsaturated ketones or esters **7**–**20** in excellent to modest yields (eq 1; Chart I; Table I). These products appear to be produced by elimination of nitrous acid from the initially formed C-alkylation products which we initially expected. From the results shown in Table I and other observations, the following six points deserve attention. (1) Nitro-containing products were not formed in all cases. (2) Only one of the two R^1COCH_2 groups in **1**–**6** was consumed, and R^1COCH_3 was another product obtained in a comparable yield with that of the coupling product. (3) A 2 mol equiv portion of the nitronate anion was necessary for completion of the reaction; 1 mol equiv of the corresponding nitroalkane was recovered. (4) Dipolar aprotic solvents like DMF and DMSO were superior to less polar aprotic or polar protic solvents such as THF and EtOH (entry 1). (5) Tertiary nitronate anions gave better results than secondary ones, especially when R^1 was a phenoxy group (entries 10, 11, 13, and 14). (6) The relative reactivity of bis(organo)tellurium dichlorides used was in the order of **2** > **1** > **3** > **6** > **5** ≈ **4** (entries 1, 5, 6, and 8–10), reflecting the decreasing order of electron-withdrawing ability of R^1 and the steric hindrance by the *t*-Bu group. Indeed, kinetic competition reactions among **1**–**3** toward $LiCMe_2NO_2$ showed that the more electron-withdrawing the para substituent on the phenyl ring, the faster the coupling reaction (relative rate: *p*-Cl:H:*p*-OMe = 1.3:1.0:0.4).

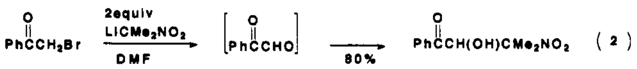


$$(R^1\overset{\overset{O}{\|}}{C}CH_2)_2TeCl_2 + \overset{LiO}{{}^{-}O}\!\!>\!\overset{+}{N}{=}C\!<\!\overset{R^2}{R^3} \xrightarrow{DMF} R^1\overset{\overset{O}{\|}}{C}CH{=}C\!<\!\overset{R^2}{R^3} + R^1\overset{\overset{O}{\|}}{C}CH_3 \qquad (1)$$

7 - **20**

1: R^1=Ph
2: R^1=4-ClC_6H_4
3: R^1=4-$MeOC_6H_4$
4: R^1=t-Bu
5: R^1=MeO
6: R^1=PhO

It was found that the reaction of anions derived from α-nitro ketones and esters, malonic acid esters, malononitrile, and β-keto esters with **1** failed to give any coupling product even at elevated temperature, resulting in only decomposition of **1**. Further, in the S_N2 reaction of 2 equiv of $LiCMe_2NO_2$ with phenacyl bromide in DMF, O-alkylation occurred exclusively to provide 2-hydroxy-3-methyl-3-nitro-1-phenyl-1-butanone via phenylglyoxal (eq 2). These results suggest that the coupling reaction shown in eq 1 proceeds by an unusual reaction pathway quite different from the ordinary S_N2 reaction.



$$Ph\overset{\overset{O}{\|}}{C}CH_2Br \xrightarrow[DMF]{2equiv\ LiCMe_2NO_2} \left[Ph\overset{\overset{O}{\|}}{C}CHO\right] \xrightarrow[80\%]{} Ph\overset{\overset{O}{\|}}{C}CH(OH)CMe_2NO_2 \qquad (2)$$

Other organotellurium chlorides were subjected to the reaction with $LiCMe_2NO_2$ in DMF. Bis(phenethyl)tellu-

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(8) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.

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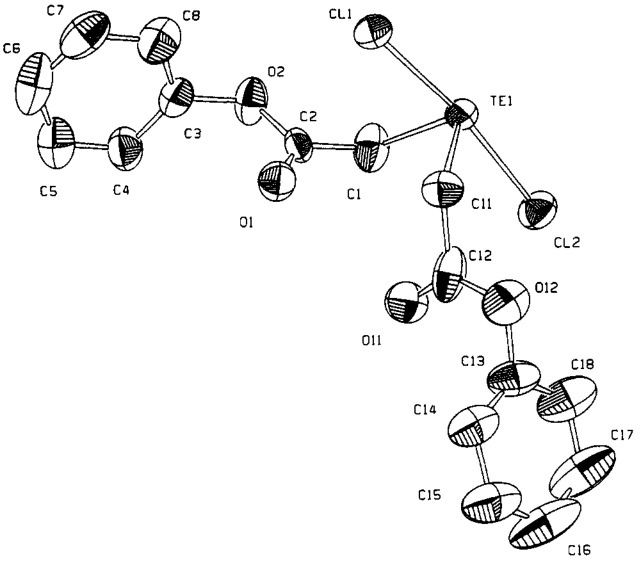
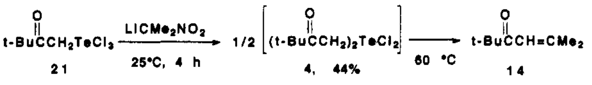


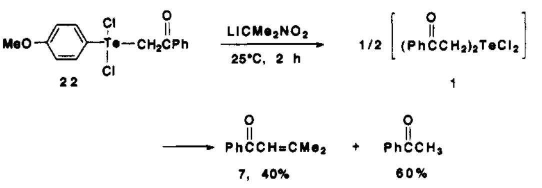
Figure 1. ORTEP drawing of compound 6.

rium dichloride [$(PhCH_2CH_2)_2TeCl_2$] afforded phenethyl chloride and styrene at 60 °C without forming any coupling product. α-(Trichlorotelluro)pinacolone (*t*-BuCO-CH_2TeCl_3; **21**) failed to give **14** at 25 °C, but instead partial disproportionation of **21** occurred to lead to **4** in a 44% yield based on the recovered *t*-$BuCOCH_2$ group (eq 3).



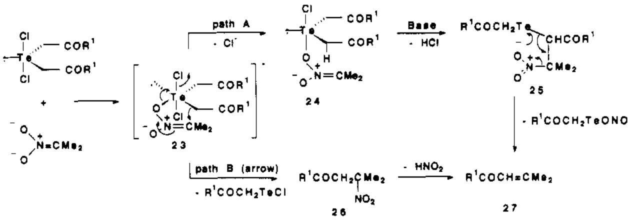
$$\underset{\textbf{21}}{t\text{-}Bu\overset{O}{\overset{\|}{C}}CH_2TeCl_3} \xrightarrow[25\,°C,\ 4\ h]{LiCMe_2NO_2} 1/2\ \underset{\textbf{4},\ 44\%}{\left[(t\text{-}Bu\overset{O}{\overset{\|}{C}}CH_2)_2TeCl_2\right]} \xrightarrow[60\ °C]{} \underset{\textbf{14}}{t\text{-}Bu\overset{O}{\overset{\|}{C}}CH{=}CMe_2} \quad (3)$$

The same reaction at 60 °C afforded the coupling product **14** probably through **4**. α-[Dichloro(*p*-methoxyphenyl)-telluro]acetophenone ($(MeOC_6H_4)(PhCOCH_2)TeCl_2$; **22**)[6] reacted with 2 equiv of $LiCMe_2NO_2$ to produce **7** in 40% yield along with acetophenone (60%); presumably, disproportionation of **22** into **1** is responsible for the less than 50% yield of **7** (eq 4). Contrary to the reaction of nitronate anions with triphenylbismuthonium dichloride (Ph_3BiCl_2),[4] diphenyltellurium dichloride (Ph_2TeCl_2) was inert to the above coupling reaction conditions even at elevated temperature. Thus, a combination of the symmetrical bis(organo)tellurium dichlorides bearing two carbonyl functions on the α- and α′-carbons to the tellurium and nitronate anions was essential for successful coupling reaction. Although α,β-unsaturated ketones and esters **7–22** are available by other methods such as the Wittig reaction of phosphorus ylides with aldehydes or ketones,[12] methodology described here would be synthetically useful in view of the ready availability of a variety of aliphatic nitro compounds[7,13] and the compatibility of a remote keto group in the nitro compound as shown in entry 7 of Table I.



(4)

Scheme I



In order to investigate the reaction mechanism, the reaction of **1** with $LiCMe_2NO_2$ was subjected to radical diagnoses.[8] Consequently, the reaction was not inhibited at all by the addition of radical scavengers such as *m*-dinitrobenzene and di-*tert*-butylnitroxide nor accelerated by visible and UV light irradiation, so radical mechanism can be excluded. Therefore, we considered that coupling reaction shown in eq 1 would occur by a polar mechanism that is initiated by coordination of the nitronate oxygen atom to the tellurium. To know the exact structure of **1–6**, we decided to perform an X-ray analysis of bis(organo)-tellurium dichlorides used. Among the six tellurium complexes, we could obtain single crystal of only **6**, and its ORTEP drawing was shown in Figure 1. Interestingly, an intramolecular interaction between the carbonyl oxygen of an $PhOCOCH_2$ group and the tellurium was not observed; the intramolecular distance between the tellurium atom and the carbonyl oxygen is longer than the sum of the van der Waals radii (3.60 Å) of Te and O. The X-ray structure shows that the chlorine atoms are disposed in the apical position of the distorted trigonal bipyramid and both $PhOCOCH_2$ groups are directed toward the outside in the equatorial position. Apparently, **6** possesses a vacant coordination site open to external nitronate oxygen atom. This result was quite different from that of 2-[dichloro-(*p*-methoxyphenyl)telluro]cyclohexanone [$(MeOC_6H_4)$-$(C_6H_9O)TeCl_2$], where an interaction between the tellurium atom and the carbonyl oxygen was indicated by an X-ray analysis.[14] Probably, **21** and **22** would also have intramolecularly coordinated structures,[15] and this pentavalent structure might be responsible for their low reactivity, leading to the disproportionation of **21** and **22** to **4** and **1**, respectively, so as to react with the nitronate anion.

From these results, we propose the reaction mechanism as illustrated in Scheme I. The reaction would occur by initial coordination of the nitronate oxygen atom to the tellurium[16] to form the pentavalent complex **23**, followed by either intramolecular substitution of one chlorine atom by the oxygen atom to form the tetravalent complex **24** (path A) or intramolecular rearrangement of **23** (see arrow) to lead directly to the substitution product **26** (path B). The acidic α-carbonyl proton of complex **24** was abstracted by another molecule of $LiCMe_2NO_2$ with sufficient basicity, and intramolecular allylic type substitution occurred to form **25**, which underwent intramolecular elimination of the nitro and tellurium moieties to form **27**. Path A is more plausible than path B, since the use of basic tertiary nitronate anions and electron-withdrawing substituents R^1 led to the smooth reaction giving the desired products **27** in high yields, and **26** was never detected.

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[12] For a recent comprehensive review of the Wittig reaction, see: Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.

[13] Ono, N. In *Nitro Compounds; Recent Advances in Synthesis and Chemistry*; Feuer, H., Nielsen, A. T., Eds.; VCH Publishers: New York, 1990; p 1.

[14] Zukerman-Schpector, J.; Castellano, E. E.; Comasseto, J. V.; Stefani, H. A. *Acta Crystallogr.* **1988**, *C44*, 2182.

[15] As an analogous example, an X-ray analysis of (*cis*-2-ethoxycycloheptyl)tribromotellurium (IV) showed that the structure is a distorted octahedron owing to the intramolecular coordination of the oxygen atom of the ethoxy group to the tellurium atom. Cameron, T. S.; Amero, R. B.; Chan, C.; Cordes, R. E. *Cryst. Struct. Commun.* **1980**, *9*, 543.

[16] See ref 2d.

Conclusions

The coupling reaction described here unveiled a new aspect of reactivity of bis(organo)tellurium dichlorides. Namely, the ambident nucleophilicity of nitronate anions and the Lewis acidity or hypervalency of tellurium atom in bis(organo)tellurium dichlorides interplay to provide a mechanistically intriguing coupling reaction. We proposed a plausible reaction mechanism consistent with all experimental results. This is the first report that organotellurium chlorides were used as the electrophile for a new C–C bond forming reaction.

Experimental Section

Infrared spectra were recorded as liquid films on NaCl plates or as KBr pellets, using a Jasco IR-810 spectrophotometer. NMR spectra were obtained in $CDCl_3$ solutions containing internal TMS standard on JEOL PMX-60 Si or GSX-270 spectrometers. Mass spectra were obtained on a Hitachi M-80 instrument. Elemental analyses were performed by the Ehime University Advanced Instrumentation Center for Chemical Analysis. All reactions were run under argon. DMF was distilled from CaH_2.

Lithium nitronates were prepared by reacting the corresponding nitroalkanes or allylic nitro compounds[17] (1.05 equiv) with lithium methoxide (1.0 equiv) in methanol at 25 °C for 2 h, followed by evaporating methanol, washing the resulting salts with *n*-pentane, and drying in vacuo, and used without further purification. Bis(acylmethyl)tellurium dichlorides **1**–**4**[5] and α-[dichloro(*p*-methoxyphenyl)telluro]acetophenone **22**[6] were prepared by literature methods. α-(Trichlorotelluro)pinacolone (**21**) was similarly prepared from equimolecular amounts of pinacolone and $TeCl_4$.[5d] Bis[(alkoxycarbonyl)methyl]tellurium dichlorides **5** and **6** were prepared in 70–75% yield by reacting the corresponding ketene silyl acetals with $TeCl_4$ in ether at 25 °C according to the method for preparation of **1**.[5c] According to a general procedure,[18] bis(phenethyl)tellurium dichloride was prepared by chlorination with SO_2Cl_2 of bis(phenethyl) telluride in *n*-hexane at 25 °C, which was synthesize from Na_2Te and $PhCH_2CH_2Br$ in aqueous dioxane, and purified by recrystallization from benzene/*n*-hexane. Spectral data for new compounds are listed below.

4: mp 191–192 °C; IR (KBr) 1690, 1375, 1060, 1000 cm^{-1}; ^{1}H NMR δ 4.82 (s, 4 H), 1.25 (s, 18 H); ^{13}C NMR δ 208.4, 57.4, 44.1, 26.4. Anal. Calcd for $C_{12}H_{22}O_2Cl_2Te$: C, 36.32; H, 5.59. Found: C, 36.42; H, 5.40.

5: mp 50–55 °C; IR (KBr) 1700, 1425, 1270, 1110, 1095 cm^{-1}; ^{1}H NMR δ 4.42 (s, 6 H), 3.87 (s, 4 H); ^{13}C NMR δ 166.15, 53.77, 47.58. Anal. Calcd for $C_6H_{10}O_4Cl_2Te$: C, 20.70; H, 2.96. Found: C, 20.91; H, 2.92.

6: mp 109–112 °C; IR (KBr) 1725, 1240, 1180, 1075, 685 cm^{-1}; ^{1}H NMR δ 4.69 (d, J = 0.9 Hz, 4 H), 7.44–7.19 (m, 10 H); ^{13}C NMR δ 164.28, 150.22, 129.69, 126.84, 121.39, 47.28. Anal. Calcd for $C_{16}H_{14}O_4Cl_2Te$: C, 40.99; H, 3.01. Found: C, 40.83; H, 3.04.

21: mp 114–115 °C; IR (KBr) 1700, 1640 cm^{-1}; ^{1}H NMR δ 5.44 (s, 4 H), 1.31 (s, 18 H). Anal. Calcd for $C_6H_{11}C_{13}Te$: C, 21.63; H, 3.33. Found: C, 21.68, H, 3.27.

Bis(phenethyl)tellurium Dichloride: mp 75–78 °C; IR (KBr) 1500, 1460, 760, 740, 705 cm^{-1}; ^{1}H NMR δ 7.32 (br s, 10 H), 3.74 (d, J = 7.0 Hz, 4 H), 3.51 (d, J = 7.0 Hz, 4 H). Anal. Calcd for $C_{16}H_{18}Cl_2Te$: C, 47.01; H, 4.44. Found: C, 46.85; H, 4.55.

General Procedure for Reaction of Organotellurium Compounds with Lithium Nitronates. To the lithium nitronate (4.0 mmol) in DMF (10 mL) under argon was added a DMF (10 mL) solution of the tellurium compound (2.0 mmol). The reaction mixture was stirred at 25–70 °C for the stated period of time (Table I) and then poured into 5% hydrochloric acid solution (30 mL). The aqueous mixture was filtered through Celite, extracted with ether (3 × 30 mL), washed with brine (3 × 30 mL) and water (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel.

7:[19] IR (neat) 1650, 1600, 1445, 1240, 1000 cm^{-1}; ^{1}H NMR δ 7.96–7.91 (m, 2 H), 7.56–7.42 (m, 3 H), 6.76–6.74 (m, 1 H), 2.21 (d, J = 1.2 Hz, 3 H), 2.02 (d, J = 1.2 Hz, 3 H); mass spectrum, *m/e* 160 (p).

8:[20] ^{1}H NMR δ 7.84–7.40 (m, 5 H), 7.15–6.72 (m, 2 H), 1.89 (d, J = 5.2 Hz, 3 H).

9: E/Z = 1/1; IR (neat) 1660, 1620, 1600, 1455, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.01–7.84 (m, 4 H), 7.54–7.19 (m, 6 H), 6.84 (m, 0.5 H), 6.71 (m, 0.5 H), 4.01 (s, 1 H), 3.54 (s, 1 H), 2.16 (s, 1.5 H), 1.90 (s, J = 1.22 Hz, 1.5 H). Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.28; H, 6.85.

10:[21] IR (neat) 2925, 1710, 1670, 1600 cm^{-1}; ^{1}H NMR δ 7.97–7.92 (m, 2 H), 7.57–7.39 (m, 4 H), 6.85 (dd, J = 15.3, 0.6 Hz, 1 H), 6.29 (m, 1 H), 2.27–2.24 (m, 4 H), 1.76–1.60 (m, 4 H); mass spectrum, *m/e* 212 (p).

11:[22] IR (neat) 1660, 1610, 1595, 1245, 1000 cm^{-1}; ^{1}H NMR δ 7.89–7.84 (m, 2 H), 7.43–7.38 (m, 2 H), 6.70 (m, 1 H), 2.21 (d, J = 1.2 Hz, 3 H), 2.02 (d, J = 1.2 Hz, 3 H); mass spectrum, *m/e* 194 and 195 (p).

12:[22] IR (neat) 1660, 1600, 1250, 1170, 825 cm^{-1}; ^{1}H NMR δ 7.95–7.90 (m, 2 H), 6.95–6.90 (m, 2 H), 6.70 (m, 1 H), 3.86 (s, 3 H), 2.18 (d, J = 1.2 Hz, 3 H), 2.00 (d, J = 1.2 Hz, 3 H); mass spectrum, *m/e* 190 (p).

13: E/Z = 2/1; IR (neat) 1710, 1600, 1450, 1360, 1240 cm^{-1}; ^{1}H NMR δ 8.06–7.83 (m, 2 H), 7.57–7.39 (m, 3 H), 6.78 (d, J = 1.2 Hz, $^1/_3$ H), 6.72 (q, J = 1.2 Hz, $^2/_3$ H), 2.82–2.50 (m, 4 H), 2.20 (s, 3 H), 2.18 (d, J = 1.2 Hz, $^2/_3$ H), 2.02 (d, J = 1.2 Hz, $^1/_3$ H). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.68; H, 7.55.

14:[23] IR (neat) 2945, 1670, 1615, 1470, 1100 cm^{-1}; ^{1}H NMR δ 6.31 (m, 1 H), 2.11 (d, J = 1.2 Hz, 3 H), 1.91 (d, J = 1.2 Hz, 3 H), 1.14 (s, 9 H). **16**: IR (neat) 1730, 1655, 1220, 1125, 1070 cm^{-1}; ^{1}H NMR δ 7.41–7.34 (m, 2 H), 7.26–7.18 (m, 1 H), 7.12–7.07 (m, 2 H), 5.92 (m, 1 H), 2.23 (d, J = 1.2 Hz, 3 H), 1.99 (d, J = 1.2 Hz, 3 H); mass spectrum, *m/e* 176 (p).

15:[24] ^{1}H NMR δ 5.61–5.69 (m, 1 H), 3.68 (s, 3 H), 2.17 (d, J = 1.2 Hz, 3 H), 1.90 (d, J = 1.2 Hz, 3 H); mass spectrum, 4*m/e* 114 (p).

16:[25] IR (neat) 1730, 1655, 1220, 1125, 1070 cm^{-1}; ^{1}H NMR δ 7.41–7.07 (m, 5 H), 5.92 (m, 1 H), 2.23 (d, J = 1.2 Hz, 3 H), 1.99 (d, J = 1.2 Hz, 3 H); mass spectrum, *m/e* 176 (p).

17:[26] IR (neat) 1720, 1640, 1180, 1140, 950 cm^{-1}; ^{1}H NMR δ 7.41–7.34 (m, 2 H), 7.25–7.09 (m, 4 H), 6.04 (dq, J = 15.3, 1.5 Hz, 1 H), 1.97 (dd, J = 7.0, 1.5 Hz, 3 H); mass spectrum, *m/e* 162 (p).

18: E/Z = 1/1; IR (neat) 1735, 1640, 1600, 1495, 1125 cm^{-1}; ^{1}H NMR δ 7.43–7.07 (m, 10 H), 6.01 (s, 0.5 H), 5.90 (q, J = 1.2 Hz, 0.5 H), 4.08 (s, 1 H), 3.51 (s, 1 H), 2.19 (d, J = 1.2 Hz, 1.5 H), 1.89 (d, J = 1.2 Hz, 1.5 H). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.77; H, 6.54.

19: E/Z = 8/3; IR (neat) 1725, 1620, 1590, 1480, 1190 cm^{-1}; ^{1}H NMR δ 9.39–7.06 (m, 6.27 H), 6.61 (m, 0.27 H), 6.25 (m, 0.73 H), 5.95 (d, J = 15.6 Hz, 0.73 H), 2.29–2.21 (m, 4 H), 1.77–1.64 (m, 4 H). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.85; H, 7.13.

20: E/Z = 7/3; IR (neat) 1740, 1590, 1200, 1125 cm^{-1}; ^{1}H NMR δ 7.40–7.05 (m, 5 H), 6.30 (t, J = 7.0 Hz, 0.3 H), 6.03 (s, 0.3 H), 5.73 (s, 0.7 H), 5.71 (t, J = 6.4 Hz, 0.7 H), 2.43–1.46 (m, 13 H). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.50; H, 8.06.

2-Hydroxy-3-methyl-3-nitro-1-phenyl-1-butanone: IR (KBr) 3450, 1665, 1540, 1345, 700 cm^{-1}; ^{1}H NMR δ 7.93–7.50 (m, 5 H), 5.60 (d, J = 8.2 Hz, 1 H), 3.97 (d, J = 8.2 Hz, 1 H), 1.55

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Table II. Crystallographic Data for Compound 6

formula	$C_{16}H_{14}O_4Cl_2Te$
cryst color	coloreless
a, Å	9.769 (3)
b, Å	6.188 (4)
c, Å	28.58 (1)
V, Å^3	1728 (4)
space group	$Pna2_1$
Z	4
dens (calc), g/cm^3	1.802
$F(000)$	912
cryst dimens, mm	0.15 × 0.15 × 0.30
diffractometer	Rigaku (AFC-5R)
radiation (λ, Å)	Mo Kα (0.71069)
μ, cm^{-1}	20.51
scan type	ω
scan rate, deg/min	8
transmissn factor	0.73-1.36
empirical absn correction	using DIFABS program^a
hkl ranges	$0 \le h \le 12$, $0 \le k \le 8$, $-36 \le l \le 0$
2θ range, deg	38.4-43.7
temp, °C	25
no. of unique data	2355
no. of obsd data ($I > 3\sigma(I)$)	1482
no. of variables	263
R, R_w^{b}	0.034, 0.039
largest peak, e/Å^3	1.59
goodness of fit	1.75

^{a}Reference 31. $^b R = (\Sigma||F_o| - |F_c||)(\Sigma|F_o|)^{-1}$; $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$.

Table III. Selected Bond Distances (Å) and Angles (deg) for 6

Bond Distances			
Te(1)-Cl(1)	2.515 (2)	Te(1)-C(1)	2.14 (1)
Te(1)-Cl(2)	2.507 (3)	Te(1)-C(11)	2.12 (1)
Bond Angles			
Cl(1)-Te(1)-Cl(2)	172.89 (7)	Cl(2)-Te(1)-C(1)	86.3 (3)
Cl(1)-Te(1)-C(1)	88.8 (3)	Cl(2)-Te(1)-C(11)	89.7 (3)
Cl(1)-Te(1)-C(11)	85.9 (3)	C(1)-Te(1)-C(11)	97.3 (4)

Table IV. Positional Parameters and Isotropic Thermal Parameters (Å^2) for 6

atom	x	y	z	B(eq)^a
Te(1)	0.15290 (5)	0.12842 (7)	0	2.96 (2)
Cl(1)	0.3527 (3)	0.1016 (4)	0.05519 (9)	3.9 (1)
Cl(2)	−0.0479 (3)	0.1051 (4)	−0.05442 (9)	4.1 (1)
O(1)	0.2071 (8)	−0.389 (1)	0.0510 (2)	4.2 (3)
O(2)	0.1166 (8)	−0.234 (1)	0.1152 (3)	4.3 (3)
O(11)	0.0953 (8)	−0.385 (1)	−0.0534 (3)	4.8 (4)
O(12)	0.186 (1)	−0.218 (2)	−0.1154 (3)	5.5 (4)
C(1)	0.044 (1)	−0.096 (2)	0.0435 (4)	4.6 (5)
C(2)	0.137 (1)	−0.251 (2)	0.0674 (4)	3.1 (4)
C(3)	0.189 (1)	−0.386 (2)	0.1439 (4)	3.9 (5)
C(4)	0.135 (1)	−0.589 (3)	0.1522 (5)	4.6 (6)
C(5)	0.204 (1)	−0.724 (2)	0.1795 (4)	5.4 (6)
C(6)	0.323 (1)	−0.658 (3)	0.2023 (4)	6.4 (7)
C(7)	0.375 (1)	−0.461 (3)	0.1935 (5)	6.1 (7)
C(8)	0.309 (1)	−0.316 (2)	0.1631 (4)	5.5 (6)
C(11)	0.258 (1)	−0.103 (2)	−0.0414 (4)	3.8 (4)
C(12)	0.168 (1)	−0.258 (3)	−0.0717 (5)	4.8 (6)
C(13)	0.108 (1)	−0.359 (2)	−0.1446 (4)	5.0 (6)
C(14)	0.158 (1)	−0.554 (4)	−0.1542 (6)	6.1 (8)
C(15)	0.090 (2)	−0.678 (3)	−0.1897 (5)	7.6 (9)
C(16)	−0.028 (2)	−0.595 (4)	−0.2094 (5)	9 (1)
C(17)	−0.077 (1)	−0.395 (3)	−0.1966 (5)	8 (1)
C(18)	−0.008 (1)	−0.276 (3)	−0.1641 (4)	6.6 (7)
H(1A)	−0.0068	−0.0167	0.0670	7.2 (5)
H(1B)	−0.0218	−0.1733	0.0249	9.3 (4)
H(4)	0.0465	−0.6212	0.1379	4.1 (7)
H(5)	0.1720	−0.8680	0.1852	6.1 (5)
H(6)	0.3664	−0.7591	0.2238	7.9 (5)
H(7)	0.4598	−0.4184	0.2076	9.9 (4)
H(8)	0.3447	−0.1741	0.1574	5.8 (5)
H(11A)	0.3191	−0.0269	−0.0625	5.3 (6)
H(11B)	0.3137	−0.1908	−0.0214	6.7 (5)
H(14)	0.2307	−0.6265	−0.1374	11.6 (3)
H(15)	0.1302	−0.8129	−0.2015	12.7 (3)
H(16)	−0.0856	−0.6879	−0.2300	14.4 (3)
H(17)	−0.1595	−0.3404	−0.2115	10.8 (3)
H(18)	−0.0416	−0.1288	−0.1546	8.9 (4)

^{a}B(eq) = $^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab \cos \gamma + B_{13}ac \cos \beta + B_{23}bc \cos \alpha)$.

(s, 3 H), 1.45 (s, 3 H). Anal. Calcd for $C_{11}H_{13}O_4N$: C, 59.19; H, 5.87; N, 6.27. Found: C, 60.03; H, 6.25; N, 5.99.

Competition Reaction. A 5-fold excess of pairs of tellurium compounds (2.5 mmol each of **1**–**3**) was subjected to the reaction with $LiCMe_2NO_2$ (1.0 mmol) in DMF (10 mL). After the usual workup, the product ratio was determined by gas chromatography of the crude products.

Crystallographic Analysis of 6. The sample was recrystallized from dichloromethane–hexane. The crystal was not of high quality and was mostly dendroid twins. Therefore, a suitable crystal of **6** was obtained by cutting the large one. It was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 38.40° < 2θ < 43.66°. Structure solutions and refinements were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.[27] Neutral atom scattering factors were taken from Cromer and Waber.[28] Anomalous dispersion effects were included in F_c.[29] The structure was solved by a combination of the Patterson method and direct methods.[30] The non-hydrogen atoms were refined anisotropically. The crystal data are summarized in Table II. Selected bond distances and angles are given in Table III. Table IV contains the atomic coordinates.

Registry No. **1**, 36362-83-1; **2**, 99766-32-2; **3**, 66839-13-2; **4**, 68970-19-4; **5**, 137824-22-7; **6**, 137844-95-2; **7**, 5650-07-7; **8**, 495-41-0; (*E*)-**9**, 137824-23-8; (*Z*)-**9**, 137824-24-9; **10**, 108286-76-6; **11**, 14618-90-7; **12**, 32097-05-5; (*E*)-**13**, 137824-25-0; (*Z*)-**13**, 137824-26-1; **14**, 14705-30-7; **15**, 924-50-5; **16**, 54897-52-8; **17**, 46117-37-7; (*E*)-**18**, 137824-27-2; (*Z*)-**18**, 137824-28-3; (*E*)-**19**, 137824-29-4; (*Z*)-**19**, 137824-30-7; (*E*)-**20**, 137824-31-8; (*Z*)-**20**, 137824-32-9; **21**, 68970-18-3; **22**, 67096-37-1; $PhCH_2CH_2Br$, 103-63-9; $PhCOCH_2Br$, 70-11-1; $PhCOCH(OH)CMe_2NO_2$, 137844-96-3; $LiON^-(O^-)=C(CH_3)_2$, 3958-63-2; $LiON^+(O^-)=CHCH_3$, 28735-55-9; $LiON^+(O^-)=C(CH_3)CH_2Ph$, 137824-33-0; $Ph(CH_2)_2Cl$, 622-24-2; lithium 1-cyclohexenylmethylnitronate, 137824-34-1; $LiON^+(O^-)=C(CH_3)CH_2CH_2COCH_3$, 137824-35-2; lithium 1-(1-cyclohexenyl)ethylnitronate, 137824-36-3.

Supplementary Material Available: Tables of atomic coordinates, hydrogen coordinates, bond distances and angles, and thermal parameters for **6** and figures of unit cell and packing diagrams (17 pages); tables of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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