the crude **2k** precipitated. The white precipitate was filtered and extensively washed with water. The dried material was recrystallized from ethanol and afforded 24.56 g (81%) of **2k**. For compounds **2m,n,v,w**, the reaction was carried out at room temperature overnight.

Spectral data for 2k: ^{13}C NMR ($CDCl_3$, 62.9 MHz) 170.28, 144.09, 139.94, 126.44, 125.71, 123.26, 67.25, 61.61, 59.99, 49.87, 44.07, 36.55, 21.88, 14.0, 10.29; IR (KBr disk) 3030 (w), 2970 (m), 2940 (w), 2880 (w), 1735 (s), 1470 (m), 1460 (m), 1450 (m), 1265 (s), 1230 (s), 1220 (s), 1180 (s), 755 (m), 625 (w), 585 (m) cm^{-1}. Anal. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 76.07; H, 6.74.

Methylidenemalonic Acid Diesters 3. The following generalized procedure was utilized for synthesis of the methylidenemalonic acid diesters **3** reported in Table II. The glassware was washed with HCl and flame-dried under vacuum. A two-necked, 200-mL, round-bottomed flask fitted with a thermometer, a magnetic stirrer, and a distilling apparatus was charged under nitrogen with 50 mmol of **2**, 50 mmol of powdered maleic anhydride, and 80 mL of high-boiling mineral oil (bp >190 °C under 0.2 Torr). The mixture was heated with stirring at 225 °C for 45 min and allowed to cool to room temperature. While the mixture was cooling, the maleic anhydride/anthracene adduct precipitated as a white crystalline material. Distillation of the reaction mixture under reduced pressure (see Table II) yielded **3** contaminated with a small amount of maleic anhydride (<1%), as shown by GLC analysis. Redistilled **3** was free of maleic anhydride. This procedure did not prove effective for **3v,w**.

Spectral data for 3e: ^{13}C NMR ($CDDl_3$, 62.9 MHz) 163.73, 136.57, 132.41, 69.13, 21.70; ^1H NMR ($CDCl_3$, 200 MHz) 6.42 (s, 2 H), 5.14 (heptuplet, 1 H, ^3J = 6.3 Hz), 1.30 (d, 6 H, ^3J = 6.22 Hz); IR (neat film) 2980 (m), 2940 (w), 2880 (w), 1725 (s), 1630 (w), 1470 (w), 1455 (w), 1400 (w), 1390 (m), 1375 (m), 1315 (m), 1245 (s), 1145 (m), 1100 (s) cm^{-1}; GC-MS; $M^+ + 1 = 201$.

Acknowledgment. We are grateful to UPSA Company (France) for financial support.

Synthetic Applications of Organotellurium Compounds. 1. A Facile Synthesis of α,β-Unsaturated Esters, Ketones, and Nitriles

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Received December 28, 1987

With the development of organosulfur and organoselenium compounds, there has recently been remarkable interest in the synthetic application of organotellurium compounds.[1-3] However, little attention has been paid to telluronium ylides[6,7] in comparison with sulfonium and selenonium ylides.[4,5] The nonstabilized sulfonium and selenonium ylides can react with carbonyl compounds to yield epoxides in high yields,[4,8] but the stabilized sulfonium ylides are inert to carbonyl compounds. It is significant to study the reactivity of stabilized telluronium ylides, since telluronium ylides ought to be more active than their sulfur and selenium counterparts.

Osuka and his co-workers[6] have reported the synthesis of a stabilized telluronium ylide dibutyltelluronium carbethoxymethylide, but so far there are no reports concerning dialkyltelluronium cyanomethylide (**2a**) and phenacylide (**2b**). In this paper, we shall study the synthesis and the application of these two new telluronium ylides.

Cyanomethyldibutyltelluronium chloride (**1a**) and phenacyldibutyltelluronium bromide (**1b**) can be obtained from the reaction of dibutyl telluride with chloroacetonitrile and phenacyl bromide, respectively. Compounds 1a and 1b are treated with potassium *tert*-butoxide to yield the corresponding telluronium ylides (**2a,b**), which condense easily with a variety of carbonyl compounds to yield α,β-unsaturated nitriles and ketones in moderate yields (Table I).

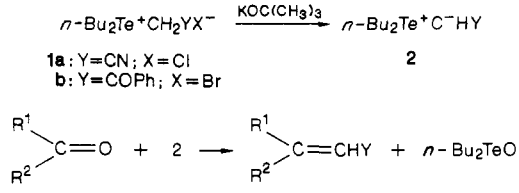

Table I. Synthesis of α,β-Unsaturated Nitriles and Ketones with Corresponding Telluronium Ylides.[a] Method A

products	% yield[b]	E/Z[c]
$C_6H_5CH{=}CHCN$	78	12/1
p-$ClC_6H_4CH{=}CHCN$	83	16/1
p-$CH_3OC_6H_4CH{=}CHCN$	60	70/1
p-$NO_2C_6H_4CH{=}CHCN$	80	18/1
p-$BrC_6H_4CH{=}CHCN$	71	25/1
o-$ClC_6H_4CH{=}CHCN$	61	124/1
p-$CH_3C_6H_4CH{=}CHCN$	78	16/1
$(CH_3)_2C{=}CHCN$	36	
c-$C_6H_{10}{=}CHCN$	49	
p-$ClC_6H_4CH{=}CHCOPh$	81	
p-$BrC_6H_4CH{=}CHCOPh$	74	

[a] All reactions were performed as described in detail in the text. [b] For isolated product. [c] Determined by ^1H NMR spectroscopy.

Table II. Synthesis of α,β-Unsaturated Esters, Ketones, and Nitriles with Corresponding Telluronium Salts.[a] Method B

	telluronium salt		
R	X	Y	% yield[b]
p-NO_2	Br	$COOCH_3$	95
m-NO_2	Br	$COOCH_3$	97
m-NO_2	Br	COPh	97
p-NO_2	Br	COPh	95
p-Cl	Br	COPh	97
p-Br	Br	COPh	96
p-NO_2	Cl	CN	88

[a] All reactions were performed as described in detail in the text. All products were found to be the *E* isomers by their melting points and IR and NMR spectra. [b] Isolated yields.

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0022-3263/88/1953-4862$01.50/0

Table III. One-Pot Synthesis of α,β-Unsaturated Esters, Ketones, and Nitriles with Dibutyl Telluride.[a] Method C

R	α-halo compounds X	α-halo compounds Y	% yield[b]
p-NO_2	Br	$COOCH_3$	85
m-NO_2	Br	$COOCH_3$	89
p-Br	Br	$COOCH_3$	76
p-NO_2	Br	$COOC_2H_5$	93
p-NO_2	Br	COPh	92
m-NO_2	Br	COPh	90
p-Cl	Br	COPh	89
p-Br	Br	COPh	86
p-NO_2	Cl	CN	83

[a] All reactions were performed as described in detail in the text. All products were found to be the *E* isomers by their melting points and IR and NMR spectra. [b] Isolated yields.

It is noteworthy that in the above reactions none of α,β-epoxy nitriles and ketones were detected, and the predominant products are *E* configurational as confirmed by the ^1H NMR spectra.

Because the above reaction was accomplished under conditions of low temperature, no oxygen, and strong base, we investigated the characteristics of organotellurium compounds further in order to explore simpler methods.

Considering the lower energy and higher polarity of the C–Te bond in organotellurium compounds, we thought that the corresponding telluronium salts might condense directly with carbonyl compounds under neutral conditions, without telluronium ylides as intermediates.

As expected, aromatic aldehydes reacted with carbethoxymethyldibutyltelluronium bromide (**1c**), phenacyldibutyltelluronium bromide (**1b**), and cyanomethyldibutyltelluronium chloride (**1a**) upon refluxing in THF under neutral conditions to afford α,β-unsaturated esters, ketones, and nitriles, respectively, in excellent yields (Table II).

$$RC_6H_4CHO + n\text{-}Bu_2Te^+CH_2YX^- \xrightarrow[\text{reflux}]{\text{THF}} RC_6H_4CH{=}CHY$$

1a: Y = CN; X = Cl
1b: Y = COPH; X = Br
1c: Y = COOR; X = Br

Because the telluronium salts can easily be prepared from dibutyl telluride and α-halo esters, ketones, or nitriles, it is possible to combine the reactions of salt formation and condensation with carbonyl compounds into a one-pot reaction.

In the presence of dibutyl telluride, methyl bromoacetate, ω-bromoacetophenone, and chloroacetonitrile condense directly with aromatic aldehydes to give α,β-unsaturated esters, ketones, and nitriles in high yields (Table III).

$$RC_6H_4CHO + Bu_2Te + XCH_2Y \xrightarrow[\text{reflux}]{\text{THF}} RC_6H_4CH{=}CHY$$

X = Br, Cl; Y = $COOCH_3$, $COOC_2H_5$, COPh, CN

It should be emphasized that the one-pot synthetic method was obviously preferred over the methods via

Table IV. Melting Points (Boiling Points) and Spectral Data of the Products Yielded from Method A

products	mp (bp), °C	lit. mp (bp), °C	IR, cm^{-1}	^1H NMR, ppm
$C_6H_5CH{=}CHCN$	(116/5 mm)	(114/5 mm)[11]	2220, 1630, 750	5.4 (d, cis), 5.84 (d, trans), 7.22–7.76 (5 H, m)
p-$ClC_6H_4CH{=}CHCN$	84–86	84–85[11]	2220, 1640, 805	5.45 (d, cis), 5.90 (d, trans), 7.3–7.48 (5 H, m)
p-$CH_3OC_6H_4CH{=}CHCN$	61–62	64[11]	2220, 1610, 810	3.8 (3 H, s), 5.2 (d, cis), 5.67 (d, trans), 6.9–7.8 (5, H, m)
p-$NO_2C_6H_4CH{=}CHCN$	196–198	200[11]	2230, 1610, 830	5.65 (d, cis), 6.0 (d, trans), 7.32–8.24 (5 H, m)
p-$BrC_6H_4CH{=}CHCN$	106–107	105–106[11]	2220, 1630, 800	5.4 (d, cis), 5.8 (d, trans), 7.16–7.56 (5 H, m)
o-$ClC_6H_4CH{=}CHCN$	38–39	40[12]	2220, 1625, 745	5.56 (d, cis), 5.88 (d, trans), 7.25–7.87 (5 H, m)
p-$CH_3C_6H_4CH{=}CHCN$	78–79	79–80[12]	2220, 1630, 800	2.36 (3 H, s), 5.32 (d, cis), 5.80 (d, trans), 7–7.76 (5 H, m)
$(CH_3)_2C{=}CHCN$	(62–65/8 mm)	(140–142)[13]	2220, 1605	1.4 (6 H, s), 2.88 (1 H, s)
c-$C_6H_{10}{=}CHCN$	(74–76/8 mm)	(82–83/10 mm)[14]	2220, 1640	0.92 (2 H, m), 1.64 (4 H, m), 2.56 (4 H, m), 2.48 (1 H, s)
p-$ClC_6H_4CH{=}CHCOPh$	103–105	103–104[15]	1670, 1610	7.40 (1 H), 7.70 (1 H), 7.48–7.76 (4 H, m), 7.92–8.12 (5 H, m)
p-$BrC_6H_4CH{=}CHCOPh$	120–122.5	123.5[16]	1670, 1615	7.41 (1 H), 7.68 (1 H), 7.38–8.02 (9 H, m)

Table V. Melting Points and Spectral Data of the Products Yielded from Method B or C

products	mp, °C	lit. mp, °C	IR, cm^{-1}	^1H NMR, ppm
p-$NO_2C_6H_4CH{=}CHCOOCH_3$	158–160	160–161[17]	1375, 1650, 1320, 1190, 825	3.76 (3 H, s), 6.50 (1 H, d), 7.70 (1 H, d), 7.60–8.24 (4 H, m)
m-$NO_2C_6H_4CH{=}CHCOOCH_3$	121–123	123–124[18]	1729, 1650, 1330	3.76 (3 H, s), 6.50 (1 H, d), 7.45–8.34 (5 H, m)
p-$BrC_6H_4CH{=}CHCOOCH_3$	81–83	80[19]	1720, 1640, 1320, 1175, 820	3.72 (3 H, s), 6.35 (1 H, d), 7.24–7.64 (5 H, m)
p-$NO_2C_6H_4CH{=}CHCOOC_2H_5$	134–136	138.5[17]	1720, 1650, 1310, 1190, 825	1.24 (3 H, t), 4.22 (2 H, q), 6.50 (1 H, d), 7.56–8.24 (5 H, m)
p-$NO_2C_6H_4CH{=}CHCOPh$	163–164	164[20]	1670, 1620	7.44 (1 H), 7.76 (1 H), 7.22–7.78 (4 H, m), 7.82–8.26 (5 H, m)
m-$NO_2C_6H_4CH{=}CHCOPh$	144–145	145[20]	1670, 1620	7.40 (1 H), 7.70 (1 H), 7.48–7.76 (4 H, m), 7.92–8.12 (5 H, m)
p-$ClC_6H_4CH{=}CHCOPh$	104–106	103–104[15]	1670, 1610	7.40 (1 H), 7.70 (1 H), 7.48–7.76 (4 H, m), 7.92–8.12 (5 H, m)
p-$BrC_6H_4CH{=}CHCOPh$	124–125	123.5[16]	1670, 1615	7.41 (1 H), 7.68 (1 H), 7.38–8.02 (9 H, m)
p-$NO_2C_6H_4CH{=}CHCN$	199	200[11]	2230, 1610, 830	6.0 (1 H, trans), 7.32–8.24 (5 H, m)

telluronium ylides as intermediates. It was not necessary to manipulate under nitrogen and at low temperature or to prepare the corresponding telluronium salt and ylide. Secondly, the total yields were also enhanced greatly. Since this reaction does not need to use a strong base, it was possible to synthesize the α,β-unsaturated compounds with base-sensitive functional groups.

Experimental Section

Synthesis of Telluronium Salts. 1. (Cyanomethyl)dibutyltelluronium Chloride. An equimolar mixture of dibutyl telluride and chloroacetonitrile was stirred under nitrogen at room temperature overnight to afford a colorless crystal: Yield 95%; mp 92–93 °C; IR (cm^{-1}) 2235 (C≡N); ^1H NMR (ppm) 1.0 (6 H, t), 1.45 (4 H, m), 2.0 (4 H, m), 3.14 (4 H, t), 3.09 (2 H, s). Anal. Found: C, 37.85; H, 6.35; N, 4.41 (theoretical values: C, 37.87; H, 6.42; N, 4.29.

2. Phenacyldibutyltelluronium Bromide. An equimolar mixture of dibutyl telluride and 2-bromoacetophenone was stirred at room temperature for 3 h to afford a colorless crystal: yield 93%; mp 104–106 °C; IR (cm^{-1}) 1665, 1610, 1590, 1455. Anal. Found: C, 43.66; H, 5.79 (theoretical values: C, 43.59; H, 5.72.

3. (Carbomethoxymethyl)dibutyltelluronium Bromide. An equimolar mixture of dibutyl telluride and methyl bromoacetate was stirred at room temperature for 3 h to afford a colorless crystal: yield 90%; mp 68–70 °C.

Synthesis of α,β-Unsaturated Esters, Ketones, and Nitriles: Typical Experimental Procedures. 1. Using Telluronium Ylides. Method A. Cyanomethyldibutyltelluronium chloride (0.34 g, 2.5 mmol) in dry THF (25 mL) was syringed into a solution of potassium *tert*-butoxide (0.43 g, 3.8 mmol) in THF at −20 °C under nitrogen. After a few minutes, the solution of *p*-chlorobenzaldehyde (0.35 g, 2.5 mmol) in THF (6 mL) was added. The mixture was stirred for 3 h at −20 °C, quenched with water, extracted with ethyl ether. The organic extract was dried and evaporated. The residue product was purified by column chromatography on silica gel to afford pure 4-chlorocinnamonitrile (83%, E/Z = 16/3).

2. Using Telluronium Salts. Method B. A mixture of carbethoxydibutyltelluronium bromide (0.99 g, 2.5 mmol) and 4-nitrobenzaldehyde (0.38 g, 2.5 mmol) was refluxed in THF (30 mL). After 6 h, it was quenched with water and extracted with ether. The organic extract was purified by recrystallization to afford pure methyl 3-(4′-nitrophenyl)propenoate (yield 95%, E configuration).

3. Using Dibutyl Telluride. Method C. A mixture of 3-nitrobenzaldehyde (0.38 g 2.5 mol), methyl bromoacetate (0.38 g, 2.5 mmol), and dibutyl telluride (0.61 g, 2.5 mmol) was refluxed in THF. After 6 h, it was worked up as method B to give pure methyl 3-(3′-nitrophenyl)propenoate (yield 89%, E configuration).

All products were confirmed by their melting points (boiling points) and IR and ^1H NMR spectra (Tables IV and V).

Acknowledgment. This research was supported by the Science Fund of the Chinese Academy of Science.

Registry No. **1a**, 111873-50-8; **1b**, 111873-49-5; **1c**, 111873-48-4; C_6H_5CH=CHCN, 4360-47-8; *p*-ClC_6H_4CH=CHCN, 28446-72-2; *p*-$CH_3OC_6H_4CH$=CHCN, 28446-68-6; *p*-$NO_2C_6H_4CH$=CHCN, 27892-88-2; *p*-BrC_6H_4CH=CHCN, 76386-57-7; *o*-ClC_6H_4CH=CHCN, 74738-21-9; *p*-$CH_3C_6H_4CH$=CHCN, 28446-70-0; $(CH_3)_2C$=CHCN, 4786-24-7; c-C_6H_{10}=CHCN, 4435-18-1; *p*-ClC_6H_4CH=CHCOPh, 956-04-7; *p*-BrC_6H_4CH=CHCOPh, 1774-66-9; C_6H_5CHO, 100-52-7; *p*-ClC_6H_4CHO, 104-88-1; *p*-$CH_3OC_6H_4CHO$, 123-11-5; *p*-$NO_2C_6H_4CHO$, 555-16-8; *p*-BrC_6H_4CHO, 1122-91-4; *o*-ClC_6H_4CHO, 89-98-5; *p*-$CH_3C_6H_4CHO$, 104-87-0; $CH_3C(O)CH_3$, 67-64-1; c-C_6H_{10}=O, 108-94-1; *p*-$NO_2C_6H_4CH$=$CHCOOCH_3$, 1608-36-2; *m*-$NO_2C_6H_4CH$=$CHCOOCH_3$, 1664-59-1; *m*-$NO_2C_6H_4CH$=CHCOPh, 614-48-2; *p*-$NO_2C_6H_4CH$=CHCOPh, 1222-98-6; *m*-$NO_2C_6H_4CHO$, 99-61-6; *n*-Bu_2Te, 38788-38-4; $ClCH_2CN$, 107-14-2; *p*-BrC_6H_4CH=$CHCOOCH_3$, 3650-78-0; *p*-$NO_2C_6H_4CH$=$CHCOOC_2H_5$, 953-26-4; $BrCH_2COOC_2H_5$, 105-36-2; ω-bromoacetophenone, 70-11-1; methyl bromoacetate, 96-32-2.

Asymmetric Synthesis of (2*R*)-2-Hydroxy-2-(2(*Z*)-octenyl)-1-cyclopentanone

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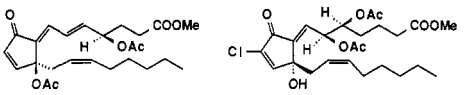
Received November 30, 1987

Marine eicosanoids such as clavulones and punaglandins are of interest because of their relationship to prostaglandins, their antitumor activity, and also the pathway of biosynthesis.[1] Recently we have achieved efficient total syntheses of (+)-clavulone II (1) and (+)-punaglandin 4 (2) utilizing (±)-2-hydroxy-2-(2(*Z*)-octenyl)-1-cyclopentanone as a key intermediate, readily obtainable from 1,2-bis[(trimethylsilyl)oxy]cyclopentene.[2c,g] In order to improve our synthetic routes to (+)-**1** and (+)-**2**, we have undertaken an efficient asymmetric synthesis of 2-hydroxy-2-(2(*Z*)-octenyl)-1-cyclopentanone, which is described in this paper.



1 2

In order to construct the quarternary carbon atom of **13** in optically pure form, it was expected that asymmetric hydride reduction of the dienone **8** would be a useful approach owing to the fact that stereocontrolled transformation of the resulting alcohol **10** into **13** would be possible. At the outset, the substrate (dienone) **8** for asymmetric reduction was synthesized by the route shown in Scheme I. Treatment of 1-[(trimethylsilyl)oxy]cyclopentene (**3**) with the α,β-unsaturated aldehyde **4** in the presence of a catalytic amount of titanium tetrachloride afforded the β-[(trimethylsilyl)oxy]cyclopentanone derivative **5**, which was deprotected to give the β-hydroxycyclopentanone **6** in 69% overall yield. Transformation of **6** to the acetate **7** followed by treatment with potassium *tert*-butoxide in THF provided the dienone **8** in 74% overall yield. The stereochemistry of **8** was supported by the following two facts. The C–H coupling constant between the carbonyl carbon and the β-hydrogen was 5 Hz, indicating that the stereochemistry of the exocyclic olefin is E.[3] Furthermore, comparison with the stereoisomer **9**, which had actually been synthesized, showed that the stereochemistry of the disubstituted olefin was Z[4] (Scheme I).

With an efficient synthesis of the dienone **8** in hand, the asymmetric hydride reduction of **8** was investigated. Reduction of **8** with the complex[5] formed from lithium aluminum hydride and "Darvon alcohol", (+)-(2*S*,3*R*)-4-(dimethylamino)-3-methyl-1,2-diphenyl-2-butanol, was carried out, affording the (*R*)-cyclopentanol derivative **10** in 78% yield with 78% ee. The enantiomeric excess of **10** thus obtained was determined by 400-MHz NMR analysis of its MTPA derivative, but the absolute configuration of **10** was not clear at this stage. Several asymmetric hydride reductions of **8** were further examined in order to improve the enantiomeric excess as well as the chemical yield. We were pleased to find that reduction of **8** with lithium aluminum hydride partially decomposed by (−)-*N*-methyl-

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0022-3263/88/1953-4864$01.50/0