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β-TRICHLOROTELLURO KETONES. PREPARATION AND EXTREMELY FACILE DEHYDROTELLURATION LEADING TO α-METHYLENE KETONES

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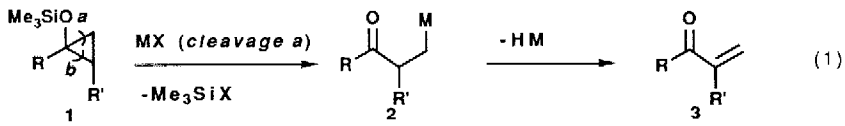
Summary: *β-Trichlorotelluro ketones **4** generated in situ from siloxycyclopropanes **1** and $TeCl_4$ react with dimethyl sulfoxide or some amines under mild conditions to provide the corresponding α-methylene ketones **3** in good yields.*

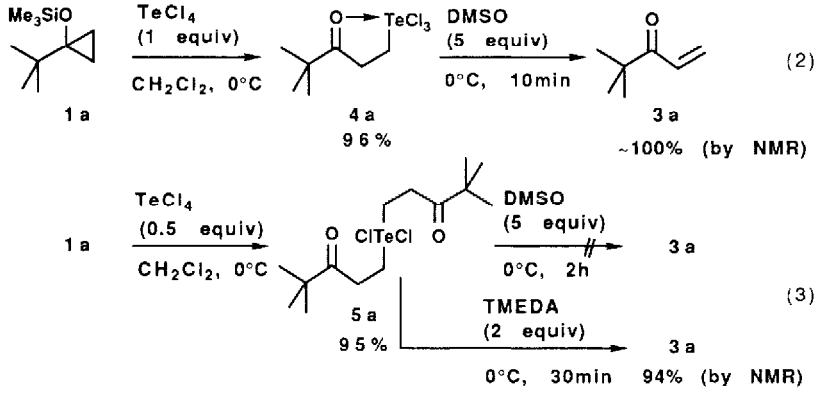
Synthetic potentiality of siloxycyclopropanes **1** largely owes to the high degree of site-selectivity in the ring-opening with electrophiles (usually at ***a*** in **1**), which ensures highly selective transformations.[1] Thus, we have designed the conversion of **1** to α-methylene ketones **3** via a β-metallo ketone formation/β-elimination sequence (eq 1).[2] In this paper, we report here that (1) β-trichlorotelluro ketones **4** were conveniently prepared from **1** and $TeCl_4$ by site-selective ring-opening of **1** at ***a*** and that (2) DMSO- or base-induced β-elimination from **4** took place quickly under mild conditions.



(1)

$TeCl_4$ readily reacted with 1 equiv of siloxycyclopropane **1a** in CH_2Cl_2 at 0 °C, giving the β-trichlorotelluro ketone **4a** in 96% yield (eq 2).[3] On the other hand, the reaction of 2 equiv of siloxycyclopropane **1a** with $TeCl_4$ gave bis(β-acylalkyl)tellurium dichloride **5a** in 95 % yield (eq 3).[4] The reaction of 2-methyl- and bicyclic siloxycyclopropanes **1c-1f** with 1 equiv of $TeCl_4$ gave **4c-4f** respectively, which resulted from site-selective *cleavage* ***a*** in **1** with no evidence of formation of products derived from

cleavage b.[5] IR spectroscopy of **4a-4f** revealed the carbonyl stretching frequencies at 1560-1624 cm^{-1}, suggesting the coordination of carbonyl oxygens to $TeCl_3$ group. On the other hand, the normal carbonyl stretching band appeared at 1686 cm^{-1} for **5a**.

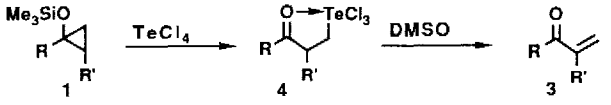


The previous observation that β-trichlorostannyl ketones having a similar intramolecular coordination undergo dehydrotrichlorostannation by DMSO (dimethyl sulfoxide)[2c] prompted us to examine the possibility of *dehydrotelluration* from **4**. Interestingly, when DMSO (5 equiv) was introduced to a solution of **4a** in CH_2Cl_2 at 0 °C, black precipitates immediately appeared and enone **3a** was formed quantitatively (eq 2).[6] The observed mildness of dehydrotelluration is in sharp contrast to the case of β-trichlorostannyl ketones, where the DMSO-promoted dehydrostannation requires heating (60 °C) for several hours (2~5 h).[2c] The dehydrotelluration of **4a** proceeded successfully in a stoichiometric fashion by use of a variety of bases including TMEDA (N,N,N',N'-tetramethylethylenediamine), Et_3N, and pyridine. On the other hand, bis(β-acylalkyl)tellurium dichloride **5a** was inert to DMSO under similar conditions (0 °C, 2 h). However, when TMEDA was used in place of DMSO, dehydrotelluration of **5a** took place effectively and both of β-acylalkyl units were converted to **3a** in 94% NMR yield (eq 3).

In order to test the generality of a β-trichlorotelluro ketone formation/dehydrotelluration protocol, other siloxycyclopropanes **1b-1f** were examined. The results are summarized in Table I. According to the one-pot procedure, α-methylene ketones **3** were conveniently prepared from **1** in high isolated yields after purification by flash chromatography.

The following procedure is typical: Siloxycyclopropane **1f** (1.34 g, 5 mmol) was added to a suspension of $TeCl_4$ (1.34 g, 5 mmol) in CH_2Cl_2 (10 mL) at 0 °C and stirred for 10 min. Then, DMSO (1.8 mL, 25 mmol) was added to this reaction mixture containing **4f** at 0 °C. After stirring at 0 °C for 10 min, black precipitates were separated by filtration and aqueous treatment (pentane/water) was carried out. The organic phase was dried ($MgSO_4$) and concentrated in vacuo. The residue was chromatographed on silica gel to give α-methylene ketone **3f** (0.903 g, 93%).

Table I. One-Pot Conversion of Siloxycyclopropanes 1 to α-Methylene Ketones 3 via β-Trichlorotelluro Ketones 4[a, b]



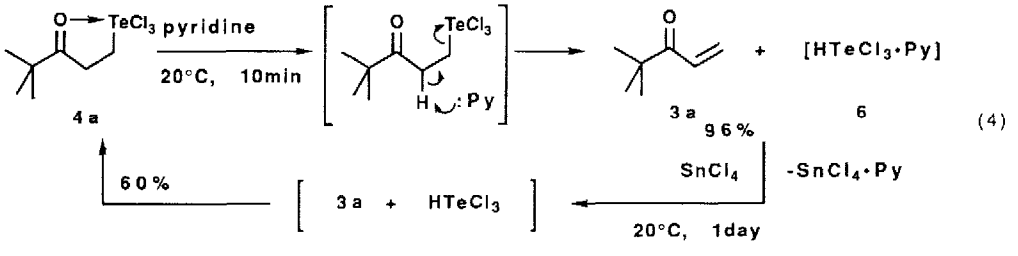
	substrate 1 R	R'	β-Te ketone 4	Isolated yield of 3 (%)[c]
1a:	$(CH_3)_3C$-	H-	4a	3a: 78
1b:		H-	4b	3b: 73
1c:	C_6H_5-	CH_3-	4c	3c: 90
1d:			4d	3d: 71
1e:	-$(CH_2)_5$-		4e	3e: 83
1f:	-$(CH_2)_{10}$-		4f	3f: 93

a) Generally reactions were carried out on a 5 mmol scale as described in the text.

b) Nearly quantitative conversion of 1 to 4 was checked by ^{1}H NMR.

c) Isolated yields from 1 after purification by flash chromatography (SiO_2).

For the dehydrotelluration the role of DMSO and amines listed above may be the one as a base to effect the elimination of 'hydrotellurium trichloride'. Thus, we suspected the resulting precipitates after dehydrotelluration of **4** to be [$HTeCl_3$•Base]. A control experiment pursued by ^{1}H NMR demonstrates that the back reaction to form β-trichlorotelluro ketone **4** does occur on treatment of the reaction mixture with Lewis acid. After 10 min of treatment of **4a** with 1 equiv of pyridine in $CDCl_3$, **4a** was completely converted to **3a** with deposition of black precipitates, but when 2 equiv of $SnCl_4$ was added to this mixture, **4a** was regenerated in 60% yield (eq 4). This result well supports the formation of $HTeCl_3$ as a pyridine complex **6** along with the formation of **3a**.



(4)

We are presently studying hydrotrichlorotelluration of enones,[7] whose results will be published in due course.

Acknowledgement

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References and Notes

(1) Murai, S.; Ryu, I.; Sonoda, N. *J. Organomet. Chem.* **1983**, *250*, 121.

(2) (a) Ryu, I.; Matumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283. (b) Ryu, I.; Ogawa, A.; Sonoda, N. *Nippon Kagaku Kaishi* **1985**, 442. (c) Ryu, I.; Murai, S.; Sonoda, N. *J. Org. Chem.* **1986**, *51*, 2389.

(3) For several recent publications describing the preparation of organotrichlorotelluro compounds, see: (a) Bäckvall, J. -E.; Bergman, J.; Engman, L. *J. Org. Chem.* **1983**, *48*, 3918. (b) Engman, L. *Organometallics* **1986**, *5*, 427. (c) Detty, M. R.; Luss, H. R.; McKelvey, J. M.; Geer, S. M. *J. Org. Chem.* **1986**, *51*, 1692. (d) Engman, L. *Organometallics* **1989**, *8*, 1997. (e) O'Brien, D. H.; Irgolic, K. J.; Huang, C. -K. *Heteroatom Chem.* **1990**, *1*, 215.

(4) Cf. Nakamura, E.; Shimada, J. -i.; Kuwajima, I. *Organometallics* **1985**, *4*, 641.

(5) IR, ^{1}H NMR (270 MHz), and ^{13}C NMR (68 MHz) data for **4a**-**4f** and **5a**: **4a**: IR (KBr) 1622 cm^{-1} (νC=O); ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9 H), 3.86-3.96 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 26.19, 34.80, 44.92, 54.73 (^1J (^{125}Te, ^{13}C) = 154.2 Hz), 228.21. **4b**: IR (neat) 1560 cm^{-1} (νC=O), 1623 cm^{-1} (νC=C); ^{1}H NMR ($CDCl_3$) δ 1.68 (m, 4 H), 2.34 (m, 2 H), 2.43 (m, 2 H), 3.90 (t, J = 7.5 Hz, 2 H, CH_2TeCl_3), 4.07 (t, J = 7.5 Hz, 2 H, $CH_2CH_2TeCl_3$), 7.56 (bs, 1 H, C=CH); ^{13}C NMR ($CDCl_3$) δ 20.70, 21.13, 22.97, 27.60, 33.32, 54.89 (^1J (^{125}Te, ^{13}C) = 148.7 Hz), 137.20, 154.05, 207.89. **4c**: IR (neat) 1566 cm^{-1} (νC=O); ^{1}H NMR ($CDCl_3$) δ 1.72 (d, J = 7.8 Hz, 3 H), 3.87 (dd, J_{vic} = 3.9 Hz, J_{gem} = 11.7 Hz, 1 H, CH_2TeCl_3), 4.26 (dd, J_{vic} = 8.3 Hz, J_{gem} = 11.7 Hz, 1 H, CH_2TeCl_3), 4.73-4.81 (m, 1 H), 7.61 (t, J = 7.7 Hz, 2 H), 7.80 (t, J = 7.7 Hz, 1 H), 8.09 (d, J = 7.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 23.04, 41.15, 61.82 (^1J (^{125}Te, ^{13}C) = 159.8 Hz), 129.62, 130.87, 132.01, 137.10, 213.05. **4d**: IR (neat) 1573 cm^{-1} (νC=O); ^{1}H NMR ($CDCl_3$) δ 2.10-2.25 (m, 1 H), 2.38-2.47 (m, 1 H), 3.12-3.31 (m, 2 H), 3.69 (dd, J_{vic} = J_{gem} = 11.2 Hz, 1 H, CH_2TeCl_3), 3.92-4.04 (m, 1 H), 4.33 (dd, J_{vic} = 7.3 Hz, J_{gem} = 11.2 Hz, 1 H, CH_2TeCl_3), 7.39-7.47 (m, 2 H), 7.69-7.61 (m, 1 H), 8.17-8.20 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.09, 30.84, 46.25, 60.24 (^1J (^{125}Te, ^{13}C) = 170.7 Hz), 127.85, 128.76, 129.48, 129.98, 138.27, 147.57, 208.39. **4e**: IR (neat) 1615 cm^{-1} (νC=O); ^{1}H NMR ($CDCl_3$) δ 1.48-2.20 (m, 8 H), 2.73-2.82 (m, 1 H), 2.96-3.04 (m, 1 H), 3.58 (dd, J_{vic} = 9.8 Hz, J_{gem} = 11.2 Hz, 1 H, CH_2TeCl_3), 3.75-3.84 (m, 1 H), 4.12 (dd, J_{vic} = 7.8 Hz, J_{gem} = 11.2 Hz, 1 H, CH_2TeCl_3); ^{13}C NMR ($CDCl_3$) δ 24.39, 27.03, 29.92, 30.47, 42.31, 51.23, 61.46 (^1J (^{125}Te, ^{13}C) = 163.1 Hz), 227.33. **4f**: IR (neat) 1624 cm^{-1} (νC=O); ^{1}H NMR ($CDCl_3$) δ 0.87-1.97 (m, 16 H), 2.15-2.33 (m, 2 H), 2.41-2.51 (m, 1 H), 3.34 (ddd, J = 4.6, 11.0, and 17.5 Hz, 1 H, CH_2 C(O)), 3.73 (dd, J_{vic} = 7.1 Hz, J_{gem} = 10.5 Hz, 1 H, CH_2TeCl_3), 3.80-3.89 (m, 1 H), 3.97 (dd, J_{vic} = 8.1 Hz, J_{gem} = 10.5 Hz, 1 H, CH_2TeCl_3); ^{13}C NMR ($CDCl_3$) δ 21.94, 22.42, 22.94, 22.96, 22.99, 24.61, 25.57, 26.06, 30.37, 37.23, 50.46, 58.00 (^1J (^{125}Te, ^{13}C) = 160.2 Hz), 227.85. **5a**: IR (KBr) 1686 cm^{-1} (νC=O); ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 18 H), 3.28 (t, J = 6.0 Hz, 4 H, CH_2TeCl_3), 3.43 (t, J = 6.0 Hz, 4 H, $CH_2CH_2TeCl_3$); ^{13}C NMR ($CDCl_3$) δ 26.45, 32.17, 38.33 (^1J (^{125}Te, ^{13}C) = 186.2 Hz), 43.83, 216.11.

(6) In contrast, the reaction of **4a** with 1 equiv of DMSO was inconveniently slow, requiring 33 h for 50% formation of **3a**. This was also experienced in the case of dehydrostannation.[2c]

(7) Cf. Hydrotrichlorostannation of enones, see: Nakahira, H.; Ryu, I.; Ogawa, A.; Kambe, N.; Sonoda, N. *Organometallics* **1990**, *9*, 277.

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