

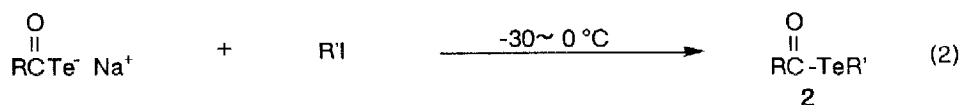
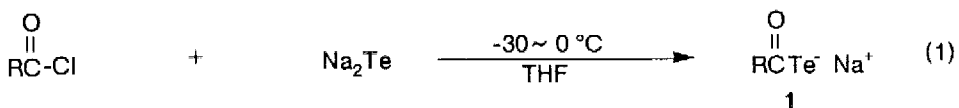
Te-ALKYL TELLUROCARBOXYLATES—  
 ISOLATION AND CHARACTERIZATION

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Summary: A series of simple alkyl tellurocarboxylates were synthesized from the sodium tellurocarboxylates and alkyl iodides, and spectroscopically characterized.

In contrast with the sulfur isologues of carboxylic acid derivatives, little has been known about the chemistry of the selenium and tellurium isologues.<sup>1</sup> Alkyl and aryl tellurocarboxylates 2 (RCOTeR') are one of the most interesting class of compounds synthetically and spectroscopically. However, their isolation has been limited to the aryl ester (2, R' = aryl), because of extreme instability towards oxygen.<sup>2</sup> Recently we succeeded in the preparation of ammonium and alkali metal tellurocarboxylates<sup>1,3</sup> which are the most important starting compounds for the synthesis of tellurocarboxylic acid derivatives. We now report a more convenient preparation of sodium tellurocarboxylates and the first isolation and characterization of a series of simple alkyl tellurocarboxylates 2.

Our continuing effort led to the direct preparation of sodium tellurocarboxylates from an equimolar reaction of acyl chlorides



with sodium telluride in tetrahydrofuran (THF). In addition, the isolation of the alkyl esters 2 was achieved by alkylation of the

Table 1. Yields and physical properties of Te-alkyl tellurocarboxylates (2)

No.	RCOTeR' R	R'	mp [°C]	Yield [%]	IR (neat) $\nu(\text{C=O})$ [cm <sup>-1</sup> ]	<sup>1</sup> H NMR (CDCl <sub>3</sub> ) $\delta$	<sup>13</sup> C NMR (CDCl <sub>3</sub> ) $\delta$
2a	PhCH <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	oil	81	1680	2.68 (Te-CH <sub>2</sub> ) 3.62 (CH <sub>2</sub> -Te)	3.5 (Te-CH <sub>2</sub> ) 203.5 (C=O)
2b	C <sub>17</sub> H <sub>35</sub>	C <sub>2</sub> H <sub>5</sub>	30 ~ 31	69	1705	2.85 (CH <sub>2</sub> -Te)	2.9 (CH <sub>2</sub> -Te)
2c	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	oil	60	1660	2.93 (Te-CH <sub>2</sub> )	202.6 (C=O) 3.6 (Te-CH <sub>2</sub> )
2d	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>5</sub>	oil	71	1660	2.88 (Te-CH <sub>2</sub> )	196.4 (C=O) 3.3 (Te-CH <sub>2</sub> )
2e	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	24 ~ 25	84	1620	1.97 (Te-CH <sub>3</sub> )	195.3 (C=O) -13.3 (CH <sub>3</sub> )
2f		<i>i</i> -C <sub>3</sub> H <sub>7</sub>	oil	74	1620	3.56 (Te-CH)	189.5 (C=O) 19.2 (Te-CH)
2g		C <sub>4</sub> H <sub>9</sub>	oil	70	1623	2.78 (Te-CH <sub>2</sub> )	191.9 (C=O) 10.6 (Te-CH <sub>2</sub> )
2h	1-Naphthyl	CH <sub>3</sub>	26 ~ 28	77	1663	2.12 (Te-CH <sub>3</sub> )	189.8 (C=O) -12.1 (Te-CH <sub>3</sub> )
2i	2-Naphthyl	C <sub>2</sub> H <sub>5</sub>	61 ~ 63	60	1655	3.05 (Te-CH <sub>2</sub> )	198.2 (C=O) 3.9 (Te-CH <sub>2</sub> ) 196.1 (C=O)

Table 2. Physical properties of the chalcogeno isologues of methyl 2-methoxybenzoate

RCOECH <sub>3</sub>		IR(neat)	<sup>1</sup> H-NMR [δ] <sup>a</sup>	<sup>13</sup> C-NMR [δ] <sup>a</sup>	
R	E	v(C=O) [cm <sup>-1</sup> ]	CH <sub>3</sub>	CH <sub>3</sub>	C=O
2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	O	1700	3.88	51.8	166.6
	S	1670	2.43	12.4	191.5
	Se	1630	2.28	5.4	192.1
	Te	1627	1.97	-13.3	189.5

a) CDCl<sub>3</sub> was used as a solvent.

sodium tellurocarboxylates with alkyl iodides, employed as both the alkylating reagent and the solvent.

For example, a solution of 2-methoxybenzoyl chloride (0.171 g, 1 mmol) in THF (8 mL) was added to freshly prepared sodium telluride (0.174 g, 1 mmol)<sup>4</sup> and the mixture was stirred at 0 °C for 1 hr.<sup>5</sup> Filtration of the reaction mixture and evaporation of the solvent in vacuo afforded sodium 2-methoxybenzenecarbotellurate 1 (R = MeOC<sub>6</sub>H<sub>4</sub>) as dark red oil in almost quantitative yield. To the sodium salt, iodomethane<sup>6</sup> (2 mL, 32 mmol) was added at -63 °C, and the mixture was stirred at -30 °C for 2 h. The dark red of the sodium salt changed to yellow within 5 min.. The excess of iodomethane was evaporated in vacuo below 0 °C. Dichloromethane (5 mL) was added, and a trace of black tellurium was filtered out. Evaporation of the solvent under reduced pressure below 0 °C yielded 0.205 g (84 %, determined by <sup>1</sup>H-NMR) of Te-methyl 2-methoxybenzenecarbotelluroate 2e as yellow crystals. Similarly, the reaction with other alkyl iodides led to high yields of the corresponding Te-alkyl alkane- or arenecarbotelluroates 2a-d, 2f-2h.<sup>3</sup> Their yields were summarized in Table 1. This is the first example of isolation of simple Te-alkyl carbotelluroates. The structures of 2 were established by Mass, IR, and <sup>1</sup>H- and <sup>13</sup>C-NMR spectra and/or microanalyses.

The obtained alkyl esters 2 are yellow to orange liquid or crystals and are relatively stable thermally and towards moisture except for the methyl esters (RCOTeCH<sub>3</sub>). They can be stored in refrigerator (-20 °C) under argon atmosphere for two weeks. Towards oxygen, however, they are very sensitive. For example, the methyl

telluroates immediately decompose on exposure to air, liberating black tellurium and unpleasant smell such as dimethyl ditelluride.

It is interesting to compare the spectral data of chalcogeno esters (RCOER: E = O, S, Se, Te). As shown in Table 2, the carbonyl stretching bands of the esters are shifted to lower frequency region in the order from E = O, S, Se, and to Te. Although the carbonyl carbon resonances ( $^{13}\text{C}=\text{O}$ ) are shifted to the down field in the order from E = O, S, and to Se, the  $^{13}\text{C}=\text{O}$  resonance of the tellurolester **2e** is observed in higher field than those of the corresponding thiol- and selenolesters. In contrast, the  $^1\text{H}$ -NMR spectra of the methyl group show the tendency of the up field shift in the order from E = O, S, Se, and to Te.

#### References and Notes

1. S. Kato, T. Murai, and M. Ishida, *Org. Prep. Proceeds. Int.*, **18**, 369 (1986).
2. Bergman and Engman reported the preparation of substituted Te-benzyl tellurocarboxylates by reduction of the corresponding bis(acyl) tellurides: J. Bergman and L. Engman, *Z. Naturforsch.*, **35b**, 217 (1980).
3. T. Kakigano, T. Kanda, M. Ishida, and S. Kato, *Chem. Lett.*, **1987**, 475.
4. F. Feher, "*Handbook of Preparative Inorganic Chemistry*," Ed. by G. Brauer, Academic Press, New York, 1963, Vol. 1, p. 441.
5. For the reaction with aliphatic acyl chlorides, the reaction temperature at  $-30\text{ }^\circ\text{C}$  is suitable.
6. The use of alkyl bromides instead of the iodides required the large prolonged reaction time: For example, the reaction of sodium 2-methoxybenzenecarbotelluroate **2e** with ethyl bromide required over 8 times of the reaction time compared with the use of ethyl iodide.

(Received in Japan 13 February 1989)