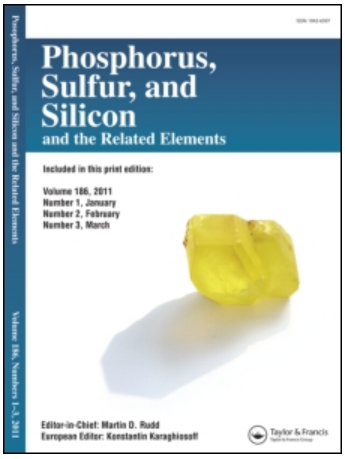

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Lithium Tellurocarboxylates: Synthesis and Characterization

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LITHIUM TELLUROCARBOXYLATES: SYNTHESIS AND CHARACTERIZATION

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A series of lithium tellurocarboxylates (**1**) were obtained as orange to red oils containing an equivalent of THF and LiCl from the reaction of acyl chlorides with lithium telluride. The salts (**1**) are extremely sensitive towards oxygen. Lithium benzenecarbotelluroate (**1d**) reacted with isopropyl iodide to give Te-isopropyl ester as main product. In contrast, the reaction of lithium telluroacetate with methyl iodide to afford 4-iodobutyl acetate in 68 % yield. The reaction mechanism discussed.

INTRODUCTION

Alkali metal tellurocarboxylates are one of the most important starting compounds for the synthesis of tellurocarboxylic acid derivatives. However, their synthesis has been limited for long time due to their extreme instability. Recently we have found that piperidinium and potassium 2-methoxybenzenecarbotelluroates are formed in the reaction of the corresponding diacyl telluride with piperidine or potassium ethanolate.[1] In addition, a convenient preparation of sodium tellurocarboxylates has been reported from the reaction of acyl chlorides with sodium telluride.[2,3] We now report the first synthesis and characterization of lithium tellurocarboxylates (**1**).

RESULTS AND DISCUSSION

For the preparation of lithium telluride which is required as starting compound, only a method using triethylborohydride and

tellurium metal has been described in literature.[4] However, in this reaction, triethylborane forms as a by-product. In order to avoid triethylborane, the direct synthesis from lithium and tellurium metals in liquid ammonia has been investigated. (eq. 1)

$$2\ Li + Te \xrightarrow[\text{liq. } NH_3]{-70\ ^\circ C,\ 7\ h} Li_2Te \qquad (1)$$

Thus, tellurium powder and two equivalents of lithium metal are stirred in liquid ammonia for 7 h.[5] Ammonia was completely evaporated at room temperature and then by heating under reduced pressure.[6] The yield of the resulting lithium telluride was almost quantitative. The obtained Li_2Te was colorless to white gray microfine crystals,[7] which are very sensitive towards oxygen.

The synthesis of lithium tellurocarboxylates was achieved through treatment of lithium telluride with an equivalent of acyl

$$RCOCl + Li_2Te \xrightarrow[\text{THF or } CH_3CN]{0\ ^\circ C,\ 2\ h} \underset{\mathbf{1}}{RCOTe^-Li^+ \cdot THF/LiCl} \qquad (2)$$

No.	R	No.	R
1a	CH_3	**1e**	$2\text{-}CH_3OC_6H_4$
1b	C_2H_5	**1f**	$4\text{-}CH_3OC_6H_4$
1c	$t\text{-}C_4H_9$	**1g**	$4\text{-}ClC_6H_4$
1d	C_6H_5		

chloride in tetrahydrofuran (THF) or acetonitrile. (eq. 2) For example, to a suspension of lithium telluride in THF, an equivalent of benzoyl chloride in THF was added dropwise under argon atmosphere and the mixture was stirred at 0 °C for 2 h. Filtration of the insoluble part and evaporation of the filtrate in vacuo gave lithium benzenecarbotelluroate (**1d**) in 94 % yield as dark red oil. The similar reaction using other acyl chlorides led to the corresponding lithium alkane- and arenecarbotelluroates (**1a–c, e–g**) in good yields. (Table 1) The

Table 1 Yields and spectral data of lithium tellurocarboxylates (**1**)

No.	$RCOTeLi \cdot (THF)_x/LiCl$ R	x	Yield [%]	^1H NMR[a] [δ]	^{13}C NMR[a] [δ]	^{125}Te NMR[a] [δ]	IR [cm^{-1}] νC=O
1a	CH_3	1	94	2.61(s, 3H, CH_3)	55.4(CH_3) 210.2(C=O)	186	1584 1504
1b	C_2H_5	1	98	0.93(t, 3H, CH_3) 2.75(q, 2H, CH_2)	11.1(CH_3) 60.4(CH_2) 208.8(C=O)	202.9	1580
1c	t-C_4H_9	0.5	96	1.07(s, 9H, CH_3)	29.1(CH_3) 55.9(CH_3-$\underline{C}$) 225.4(C=O)	77.7	1557 1485
1d	C_6H_5	1	94	7.8–8.1(m, 5H, Ar)	128–151(Ar) 211.1(C=O)	234.8	1558
1e	2-$CH_3OC_6H_4$	1	90	3.93(s, 3H, CH_3) 6.8–7.9(m, 4H, Ar)	56.7(CH_3) 112–151(Ar) 210.5(C=O)	448.8	1553
1f	4-$CH_3OC_6H_4$	1	91	3.81(s, 3H, CH_3) 6.8–8.1(m, 4H, Ar)	56.2(CH_3) 113–164(Ar) 207.1(C=O)	190.5	1550
1g	4-ClC_6H_4	1	96	7.2–8.1(m, 4H, Ar)	128–151(Ar) 207.1(C=O)	259.1	1526

[a] $CDCl_3$.

structures were established by spectral data and by conversion into Te-alkyl esters or diacyl telluride.[8]

The obtained lithium salts (**1**) are reddish orange to dark red oil containing both of an equivalent of lithium chloride and 0.5 - 1.0 equivalents of THF.[9] They are extremely sensitive towards oxygen. For example, allowing to stand in air, **1d** was quickly oxidized to give lithium benzoate with liberation of black tellurium. The salts (**1**) are readily dissolved in protic and aprotic polar solvents such as ethanol and THF, etc.

Lithium benzenecarbotelluroate (**1d**) reacts with isopropyl iodide to give the corresponding Te-isopropyl ester (**2**) as a main product. (eq. 3) In contrast, treatment of lithium telluro-

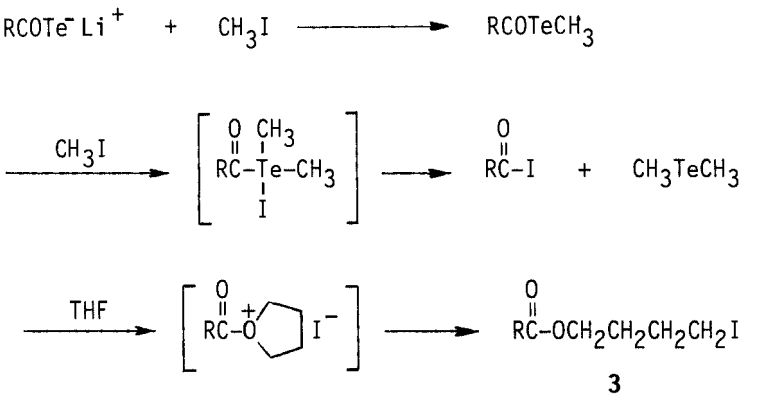
$$C_6H_5COTe^-Li^+/THF \xrightarrow[20\ °C,\ 3\ h]{i\text{-}C_3H_7I} C_6H_5COTeC_3H_7\text{-}i \quad (3)$$

2 (55 %)

$$CH_3COTe^-Li^+/THF \xrightarrow[20\ °C,\ 3\ h]{CH_3I} CH_3COOCH_2CH_2CH_2CH_2I \quad (4)$$

3a (67 %)

acetate (**1a**) with methyl iodide under the same conditions afforded 4-iodobutyl acetate (**3a**) in 67 % yield. (eq. 4)



Scheme 1

Presumably the formed Te-methyl ester would react with excess methyl iodide to lead to acyl iodide, which further reacts with tetrahydrofuran to give **3.** (Scheme 1)[10]

EXPERIMENTAL[11]

Reagents: Lithium, tellurium (powder), and acyl chlorides are reagent grade and used without further purification. Solvents were purified by the known methods and degassed before use.

Typical procedures for the preparation of lithium tellurocarboxylates (1) are described below. All procedures were carried out under argon atmosphere.

Lithium telluride. Lithium (0.320, 46 mmol) and tellurium powder (2.95 g, 23 mmol) were taken in Schlenk tube and liquid ammonia (ca. 70 ml) was added at 78 °C. After stirring at -70 °C for 6 h, evaporation of ammonia at room temperature and then at 70 - 100 °C in vacuo gave 3.26 g (99 %) of lithium telluride as colorless microfine crystals.

Lithium 4-methylbenzenecarbotelluroate (**1f**). To a suspension of freshly prepared lithium telluride (0.328 g, 2.3 mmol) in ether (5 ml), 4-methoxybenzoyl chloride (0.262 g, 1.5 mmol) in THF (5 ml) was added and the mixture was stirred at 0 °C for 1 h and then at 20 °C for 2 h. Filtration of the insoluble part and evaporation of the solvents in vacuo gave 0.54 g (91 %) of lithium 4-methoxybenzenecarbotelluroate (**1f**) as reddish orange oil.

Te-Isopropyl benzenecarbotelluroate (**2**). Isopropyl iodide (10 ml) was added dropwise to lithium benzenecarbotelluroate (**1d**) (2.05 mmol) at -46 °C and the mixture was stirred at 25 °C for 6 h. Filtration of the insoluble part, removal of the isopropyl iodide in vacuo, and then chromatography of the residue on silica gel column (CH_2CH_2/hexane = 1:3) gave 0.155 g (55%) of **2.** The IR spectrum was exactly consistent with that of the authentic sample which was prepared by the reaction of sodium benzenecarbotelluroate with isopropyl iodide.[12]

Reaction of lithium telluroacetate (**1a**) *with methyl iodide.* To lithium telluroacetate (**1a**) (17.2 mmol), methyl iodide (20 ml) was added at -46 °C, and the mixture was stirred at this temperature for 1 h and then at 0 °C for 2 h. Filtration of the insoluble part and evaporation of the methyl iodide in vacuo and

then column chromatography of the residue (silica gel, CH_2Cl_2) gave 1.37 g (67 %) of 4-iodobutyl acetate (**3a**) as colorless oil: ^{1}H-NMR ($CDCl_3$, δ) 1.70 - 2.00(m, 4H, CH_2), 2.33(s, 3H, CH_3CO), 3.23(t, 2H, CH_2I) 4.23(t, 2H, CH_2O); ^{13}C-NMR($CDCl_3$, δ) 174.8(CO), 68.5(CH_2O), 29.5(CH_3), 28.9(CH_2), 25.1(CH_2), 5.8(CH_2I); IR (neat) 1736 cm^{-1} (C=O); mass spectra (CI, m/z) 243 (M^++1).

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4. D. C. Clive, P. C. Anderson, N. Moss, and A. Signh, *J. Org. Chem.*, **47**, 1641(1982).
5. The reaction time over 7 h is required for completion of the reaction.
6. The complete removal of ammonia is required for the synthesis of lithium tellurocarboxylates.
7. Lithium telluride appears to be colorless. The white gray color of the obtained lithium telluride contains a trace of black tellurium.
8. Lithium 2-methoxybenzenecarbotelluroate (**1e**) was converted into bis(2-methoxybenzoyl) telluride.
9. One of the reasons that lithium 1,1-dimethylethanecarbotelluroate (**1c**) includes 0.5 equivalents of THF would be owing to sterically bulky t-butyl group.
10. A. Oku, T. Harada, and K. Kita, *Tetrahedron Lett.*, **22**, 681 (1982).
11. The IR spectra were measured on a PERKIN ELMER FT-IR 1640 spectrophotometer. The ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-GX-270 (270 MHz) with tetramethylsilane as an internal standard. High-resolution mass spectra were taken by a Shimadzu high-resolution mass spectrometer (GCMS 9020-DF /PAC-1100).
12. S. Kato, T. Kanda, S. Nakaiida, T. Kakigano, H. Ishihara, and T. Murai, in preparation.