A Convenient One-pot Preparation of *Te*-Alkyl Telluro-carboxylates *via* the Successive Acylation and Alkylation of Telluride Anion. Application to the Synthesis of Alkyl Telluroimidates†

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We report that successive treatment of sodium hydrogen telluride with acyl chlorides and alkyl iodides in ethanol at −15 °C under an argon atmosphere affords *Te*-alkyl telluro-carboxylates in good to moderate yields; similar treatment with *N*-tosylbenzimidoyl chloride and alkyl iodides leads to the corresponding alkyl telluroimidates as relatively unstable oils in good yields.

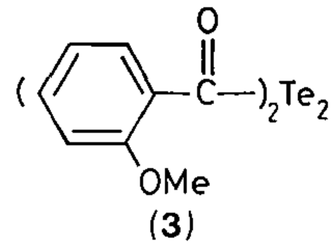
Although a variety of thio- and seleno-carboxylic acid derivatives have been described in the literature, the number of analogous tellurium compounds is limited. Known procedures for the preparation of *Te*-alkyl/*Te*-aryltelluro-carboxylates include the reaction of acyl chlorides with sodium alkyl-/aryl-tellurolates,[1] sodium telluride[2] or phenyltellurotrimethylsilane,[3] reaction of acid anhydrides with sodium alkyltellurolates,[4] alkylation of sodium telluro-carboxylates,[5] and $Co_2(CO)_8$-mediated carbonylation of diaryl ditellurides.[6] A cyclic telluroester, tellurophthalide, has also been reported.[7]

We have now developed a simple and convenient one-pot procedure for the preparation of various *Te*-alkyl telluro-carboxylates from readily available materials, acyl and alkyl halides and sodium hydrogen telluride. Thus, when an equimolar amount of an acyl chloride (**1**) was added dropwise to a solution of freshly prepared sodium hydrogen telluride in ethanol at low temperatures, the solution turned deep red. An excess of alkyl iodide was added and the resulting mixture was stirred for 1 h, allowing it gradually to attain room temperature. Usual work-up gave the corresponding *Te*-alkyl tellurocarboxylates (**2**) in 62–89% yields (Table). Acylation of hydrogen telluride anion occurred in preference to the ethanol used as the solvent. Attempts at using the sodium telluride (Na_2Te)–DMF system[8] as a tellurating agent or at using alkyl bromides as alkylating agents were unsatisfactory.

$$\underset{(\mathbf{1})}{\mathrm{RCOCl}} \xrightarrow[\mathrm{EtOH,\ -15\,^{\circ}C}]{\mathrm{NaTeH}} \xrightarrow{\mathrm{R'I}} \underset{(\mathbf{2})}{\mathrm{RCOTeR'}}$$

The reaction was smooth and clean, with neither free tellurium nor any polymeric substance being formed. However, the synthesis was subject to steric effects. Thus a hindered acid chloride such as 2,4,6-trimethylbenzoyl chloride did not react with hydrogen telluride anion under our conditions but underwent ethanolysis with the liberation of free tellurium, giving the corresponding ethyl ester.

When the deep red solution obtained by the reaction of 2-methoxybenzoyl chloride with sodium hydrogen telluride was exposed to air at room temperature, bis(2-methoxy-benzoyl) ditelluride (**3**) was obtained in 61% yield. Similar reactions with other aroyl chlorides, however, resulted in a rapid decomposition of the product and no diaroyl ditellurides could be isolated.



(**3**)

Use of *N*-tosylbenzimidoyl chloride (**4**) in place of acyl chloride in the above reaction led to the corresponding alkyl telluroimidates (**5**) in 75–92% isolated yields. These previously unreported compounds are malodorous yellow oils of low stability, which gradually decompose on storage even in a refrigerator. In contrast to the reaction of *N*-phenylbenzimidoyl chloride with sodium hydrogen selenide which produced selenobenzanilide,[9] no telluroamides[10] could be obtained under our conditions.

$$\underset{(\mathbf{4})}{\mathrm{PhC(Cl){=}NTs}} \xrightarrow[\mathrm{EtOH,\ -20\,^{\circ}C}]{\mathrm{NaTeH}} \xrightarrow{\mathrm{R'I}} \underset{(\mathbf{5})}{\mathrm{PhC(TeR'){=}NTs}}$$

In summary, the present method has the advantage that *Te*-alkyl tellurocarboxylates can be obtained in a one-pot procedure from readily available reagents. Additional advantages include mild conditions, shorter reaction times, ease of performance and work-up, and economy.

Experimental

B.p.s refer to Kugelrohr bath temperatures. IR spectra were recorded with a Hitachi 260-10 spectrophotometer while ^1H and ^{13}C NMR spectra were measured for solutions in $CDCl_3$ using a JEOL GSX 270 spectrometer. CI mass spectra were determined on a Hitachi M-80B instrument operating at 70 eV using methane as ionizing gas.

Preparation of Te-*Alkyl Tellurocarboxylates* (**2**). *Typical Procedure.*—Benzoyl chloride (0.5 mmol) in tetrahydrofuran (THF) (5 ml) was added dropwise to a stirred solution of sodium hydrogen telluride (0.5 mmol)[11] in ethanol (5 ml) at −15 °C under an argon atmosphere. The solution immediately turned deep red. Ethyl iodide (5 mmol) was added in one portion and the reaction mixture was stirred for 1 h, allowing slowly to come to room temperature. The mixture was then passed through a thin layer of Celite 545 and the filtrate was evaporated to give a crude product, which was purified by bulb-to-bulb distillation under reduced pressure, giving *Te-ethyl tellurobenzoate* (**2a**) as an oil (89%) (Found: C, 41.6; H, 4.0. $C_9H_{10}OTe$ requires C, 41.29; H, 3.85%).

Preparation of Alkyl Telluroimidates (**5**). *Typical Procedure.*—To a solution of sodium hydrogen telluride (0.5 mmol) in dry ethanol (5 ml) was added dropwise *N*-tosylbenzimidoyl chloride (0.5 mmol) in THF (5 ml) followed by ethyl iodide (5 mmol) at −20 °C under an argon atmosphere. After having been stirred for 1 h, the mixture was filtered through Celite 545 and the filtrate was evaporated *in vacuo* to give an oil, which was purified by flash chromatography on silica gel using hexane–dichloromethane as the eluent to yield *ethyl* N-*tosylbenzimidate* (**5a**) as a yellow oil (91%). Attempted distillation of this compound led only to decomposition (Found: C, 46.5;

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Table *Te*-Alkyl tellurocarboxylates (**2**) and alkyl telluroimidates (**5**)

Starting chloride	R^1	R^2	Product	Yield (%)	B.p. (°C)/mmHg	ν_{max}/cm^{-1}	δ_H ($CDCl_3$)[a]
(**1a**)	Ph	Et	(**2a**)	89	80/0.3	1720, 1650, 1570, 1440, 1195, 1165, 860, 760, 680	1.75 (3 H, t, *J* 7.6), 3.03 (2 H, q, *J* 7.6), 7.4–7.8 (5 H, m)
(**1b**)	Ph	Pr^n	(**2b**)	75	105–106/0.2	1720, 1655, 1575, 1445, 1200, 1170, 860, 760, 680	1.03 (3 H, t, *J* 7.3), 1.90 (2 H, septet, *J* 7.3), 3.06 (2 H, t, *J* 7.3), 7.4–7.8 (5 H, m)
(**1c**)	Ph	Pr^i	(**2c**)	62	115/0.2	1715, 1645, 1570, 1435, 1190, 1160, 670	1.79 (6 H, d, *J* 7.0), 3.76 (1 H, septet, *J* 7.0), 7.4–7.7 (5 H, m)
(**1d**)	n-C_7H_{15}	Et	(**2d**)	78	50/0.05	1690, 1460, 1440, 1365, 1185, 1115, 1030, 960, 780	0.88 (3 H, t, *J* 6.7), 1.2–1.4 (8 H, m), 1.64 (2 H, quintet, *J* 7.6), 1.69 (3 H, t, *J* 7.6), 2.62 (2 H, t, *J* 7.6), 2.85 (2 H, q, *J* 7.6), 3.04 (2 H, q, *J* 7.6)
(**4a**)	Ph	Et	(**5a**)	91	oil[b]	1585, 1500, 1315 1145, 1080, 880, 670	1.32 (3 H, t, *J* 7.6), 2.39 (2 H, q, *J* 7.6), 2.43 (3 H, s), 7.3–7.4 (5 H, m), 7.32 (2 H, d, *J* 8.0), 7.93 (2 H, d, *J* 8.0)
(**4b**)	4-Me-C_6H_4	Et	(**5b**)	92	oil[b,c]	1640, 1590, 1490, 1305, 1145, 1080, 830, 760, 660	1.36 (3 H, t, *J* 7.6), 2.39 (3 H, s), 2.45 (3 H, s), 2.46 (2 H, q, *J* 7.6), 7.21 (2 H, d, *J* 7.2), 7.3–7.4 (4 H, m), 7.95 (2 H, d, *J* 7.2)
(**4c**)	4-Cl-C_6H_4	Et	(**5c**)	75	oil[b,d]	1580, 1480, 1465, 1290, 1140, 1075, 685	1.33 (3 H, t, *J* 7.6), 2.41 (2 H, q, *J* 7.6), 2.42 (3 H, s), 7.3–8.0 (8 H, m)

[a]Me_4Si as internal standard; *J* values in Hz. [b]Readily decomposes on heating. [c]Found: C, 47.4; H, 4.5; N, 3.3. $C_{17}H_{19}NO_2STe$ requires C, 47.60; H, 4.46; N, 3.26%. [d]Found: C, 42.5; H, 3.6; N, 3.2. $C_{16}H_{16}ClNO_2STe$ requires C, 42.76; H, 3.59; N, 3.12%.

H, 4.3; N, 3.3. $C_{16}H_{17}NO_2STe$ requires C, 46.31; H, 4.13; N, 3.33%); *m/z* 418 ($M^+ + 1$, 0.4%), 314 (17), 285 (35), 172 (33), 155 (85), 132 (32), and 104 (100); δ_C 7.31, 15.24, 21.21, 126.24, 127.12, 127.83, 129.19, 130.51, 135.41, 141.45, 144.06, and 183.66.

Bis(2-*methoxybenzoyl*)*ditelluride* (**3**).—To a solution of sodium hydrogen telluride (0.5 mmol) was added 2-methoxybenzoyl chloride (0.5 mmol) in THF (5 ml) at −20 °C. After having been stirred for 5 min the mixture was exposed to air at room temperature. Insoluble material was removed by filtration and the solvent was evaporated off under reduced pressure to leave a dark solid, which crystallized from benzene–hexane to afford (**3**) as red needles (61%), m.p. 125–130 °C (decomp.) (lit.,[5] 130–131 °C).

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