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MILD TRANSFORMATION OF TELLURO AND SELENO ESTERS INTO CARBOXYLIC ACID AND ESTERS

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<u>ABSTRACT:</u> Te-Butyl Telluroesters and Se-Butyl Selenoesters are hydrolyzed to carboxylic acids under very mild conditions by reaction with copper(II) chloride dihydrate. When the reaction is performed in ethanol or methanol, using anhydrous copper(II) chloride a transesterification occurred leading to the oxygenated esters in good yield.

Although the preparation of telluroesters has been described in 1970 by Piette and Renson¹ only a few reports dealing with the chemical behavior of these compounds have been published to date²⁻⁷. Telluroesters are a class of compounds with promising synthetic utility. They were shown to be a good source of acyl, aroyl and carbamoyllithium intermediates which react *in situ* with different electrophiles to give α -hydroxy ketones⁵, α -hydroxyamides or α -oxoamides⁶. In addition Te-phenyl tellurobenzoate gave the corresponding phenyl alkyl ketones by reaction with lithium dialkyl cuprates³.

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In view of the synthetic potential of telluroesters and our continuous interest in the organic chemistry of tellurium, we have studied the chemical behavior of this class of compounds when treated with copper salts and other reagents.

Telluroesters (1a-f) undergo facile reaction with copper(II) chloride dihydrate in acetone at room temperature for 5 minutes affording carboxylic acids (2a-f) in good yields (Eq. 1, Table I). The products were separated by filtration from the orange solid which formed, presumably a copper-tellurium complex⁸, that was not identified.



Two selenoesters (Table I: entries 7 and 8) when treated under the same conditions were also hydrolyzed to carboxylic acids. However, carboxylic acid, esters and thioesters are inert under those conditions.

The nature of the copper salt has a dramatic influence on the reaction course. No hydrolysis products were obtained when the telluroesters 1a and 1d were treated with copper sulphate or copper(I) chloride⁹.

We also observed that when the telluroester 1a was treated with concentrated sodium hydroxide solution under reflux for two hours, no reaction occurred. On the other hand, when refluxed under acidic conditions (ethanol/sulfuric acid or ethanol/hydrochloric acid) for several hours, telluroesters 1a or 1c did not react at all.

Chalcogenoester
C ₆ H ₅ COTeC ₄ H ₉
1a
p-CH3OC6H4COTeC4H9
1b
p-ClC6H4COTeC4H9
10
C ₆ H ₅ CH ₂ COTeC ₄ H ₉
1d
CH ₃ COTeC ₄ H ₉
19
(CH ₃) ₃ CCOT ₈ C ₄ H ₉
1f
C ₆ H ₅ COSeC ₄ H ₉
3a
C ₆ H ₅ CH ₂ COSeC ₄ H ₉
3b
f isolated products; a product, not quantified.

Table I

When the reaction was performed in dry ethanol or methanol at room temperature, both selenium and tellurium esters were transformed into the corresponding oxygenated esters (Eq. 2 and Table II).



Yield (%)^a

96

74

80

65

b

73

77

68

Product

C6H5CO2H

2a p-CH₃OC₆H₄CO₂H

2b

p-ClC6H4CO2H

2c

C6H5CH2CO2H

2d

CH3CO₂H

2e

(CH₃)₃CCO₂H

2f

C₆H₅CO₂H

C6H5CH2CO2H

Table II

Chalcogenoester	R'OH	Product	Yield (%) ^a
ColleCOTeColle	CAHEOH	ColleCOoColle	85
1a	020500	4a	65
p-CH3OC6H4COTeC4H9	C ₂ H ₅ OH	p-CH3OC6H4CO2C2H5	74
16		4b	
	CH ₃ OH	p-CH3OC6H4CO2CH3	83
		4c	
	t-C₄H9OH	p-CH3OC6H4CO2C4H9	83
		4d	
p-ClC ₆ H ₄ COTeC ₄ H ₉	C₂H₅OH	p-CIC ₆ H ₄ CO ₂ C ₂ H ₅	68
1c		4e	
	CH ₃ OH	p-ClC ₆ H ₄ CO ₂ CH ₃	78
		4f	
C ₆ H ₅ CH ₂ COTeC ₄ H ₉	C ₂ H ₅ OH	C6H5CH2CO2C2H5	88
1d		4g	
	CH ₃ OH	C6H5CH2CO2CH3	72
		4h	
C6H5COSeC4H9	C ₂ H ₅ OH	$C_6H_5CO_2C_2H_5$	69
3a			
C6H5CH2COSeC4H9	C ₂ H ₅ OH	$C_6H_5CH_2CO_2C_2H_5$	73
<u>3b</u>			

a. Yield of isolated products.

The seleno and telluro esters used in this work were prepared by the reaction of the corresponding butylchalcogenate anion with acyl chloride¹⁰.

Our results show that telluro and selenoesters could serve as ester and acid protecting groups in organic syntheses. A feature of this usage must be emphasized: while alkyl esters of carboxylic acids require acidic or basic conditions for their hydrolyses, Telluro and Selenoesters can be hydrolysed to the carboxylic acids under neutral conditions. Further investigation on this scope is now in progress.

Experimental

1. Typical procedure for the preparation of telluro or selenoester:

To a suspension of elemental tellurium or selenium (5mmol) in dry THF (17ml) under a nitrogen (oxygen free) atmosphere at room temperature, a solution of Butyllithium in hexane (6mmol) was added and the mixture stirred for 15 min. in order to form the butyl chalcogenate anion intermediate. After cooling to 0 °C, the acyl chloride (5mmol) was added at once. The mixture was stirred for 30 min., diluted with ethyl acetate and washed with water. The organic phase was dried over MgSO4 and evaporated. The product was purified by flash chromatography using CCl4 as eluant.

2. Typical procedure for the preparation of carboxylic acids from Te-Butyl telluroesters:

To a solution of 1b (1.598g; 5mmol) in dry acetone (40ml) under stirring at room temperature was added CuCl₂. $2H_2O$ (1.108g; 6.5mmol). A sudden formation of a yellow-orange precipitate was observed and the reaction stirred for 5 min. The mixture was filtered, diluted with ethyl ether and washed with a 10% sodium hydroxide solution (2x 50ml). The aqueous phase was acidified with concentrated HCl and extracted with ethyl ether. The organic phase was dried over MgSO4 and evaporated. The residue was identified by ¹H-NMR, IR and CG-MS as the anysic acid.

Yield: 1.23g (77%), m.p.: 184 °C.

3. Typical procedure for the preparation of esters from Te-Butyl telluroesters:

To a solution of 1a (1.448g; 5mmol) in ethanol (20ml) under stirring and a nitrogen atmosphere at room temperature, was added anhydrous CuCl2 at once. A yellow-orange precipitate was rapidly formated, and the reaction mixture was stirred for 3 hours. Then, filtered and the solvent evaporated. The residue purified by column cromatography on silica gel using hexane:ethyl acetate (8:2) as eluant, to give ethyl benzoate.

Yield: 1.23g (85%); IR: 1786 cm⁻¹; ¹H-NMR (CCl4/TMS, δ): 1.35(t,J7,3H); 4.30(q,J7,2H); 7.2-7.6(m,3H); 7.9-8.1(m,2H).

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9. This result is in accordance with previous study on use of telluroesters as ligands in transition metal systems reported in Ref. 2.

10. Acid Chloride must be added as rapidly as possible to obtain good yields, avoiding the formation of larger amounts of dibutyl dichalcogenide.

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