Thallium(I) Carboxylates: a New Class of Reagents for the Formation of α-Iodocarboxylates

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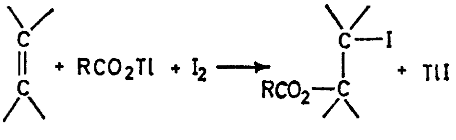
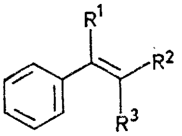
Summary Treatment of an alkene with a thallium(I) carboxylate and iodine gives the corresponding α-iodocarboxylate in high yield, thereby affording a regiospecific and inexpensive modification for the Prevost reaction.

Although α-iodocarboxylates are important in organic synthesis[1,2] few methods are available for their preparation,[3] the most satisfactory being that *via* the corresponding silver carboxylate.[2] During a search for a less expensive metal than silver for use in the Prevost reaction[2] a modification using thallium(I) carboxylates was investigated. Unlike Ag^I carboxylates, Tl^I carboxylates are readily prepared in high yield as stable crystalline solids.



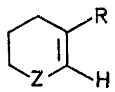
(1)

It was found that the use of a thallium(I) carboxylate and iodine provides an effective means for the high yield conversion of alkenes into the corresponding α-iodocarboxylates as indicated in reaction (1). In a typical experiment, dropwise addition of a solution of iodine in acetic acid to a solution of cyclohexene and thallium(I) acetate in acetic acid at room temperature in a stoicheiometric ratio of 1 : 1 : 1·2[4] gave a high yield of the *trans*-iodoacetate. When the reaction was carried out using a non-homogeneous system with the thallium(I) carboxylate suspended in dry benzene[2] or methylene dichloride and a stoicheiometric ratio of 1 : 1 : 2, the product was again the corresponding α-iodocarboxylate. However, with the latter system less reactive substrates (*e.g.* allylbenzene) led to intractable products. With unsymmetrical alkenes the addition was regiospecific,[5] styrene or 2-methylstyrene affording the corresponding 2-iodo-1-carboxylate. In the case of 1-methylcyclohexene and thallium(I) acetate the adduct was the unstable 2-methyl-2α-iodohex-1β-yl acetate whose structure was established from spectral evidence and conversion into more stable derivatives.



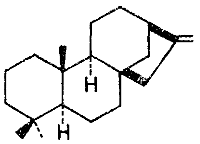
(I)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^3 = H$; $R^2 = Me$
c; $R^2 = R^3 = H$; $R^1 = Me$

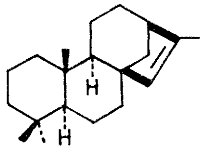


(II)

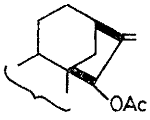
a; R = H, Z = O
b; R = Me, Z = CH_2
c; R = H, Z = CH_2



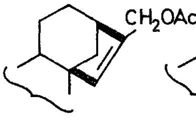
(III)



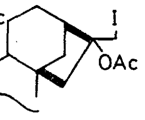
(IV)



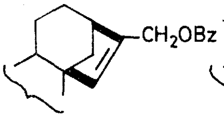
(IIIa)



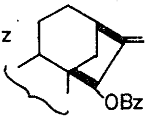
(IIIb)



(IIIc)



(IIId)



(IIIe)

Examples of the iodocarboxylation using thallium(I) acetate (Method A) and thallium(I) benzoate (Method B) are given in the Table.

TABLE

Alkene	Yields of iodocarboxylate[a] Method A[b,c]	Method B
(Ia)	98	60
(Ib)	97	66
(Ic)	98	64
(IIa)	85	85
(IIb)	90	80
(IIc)	85	81
(III)	30 (IIIa)	
	40 (IIIb)	54 (IIId)
	30 (IIIc)	46 (IIIe)
(IV)	56 (IIIb)	55 (IIId)
	38 (IIIa)	45 (IIIe)

[a] Yields recorded are of isolated material. [b] In all cases quantitative yields of TlI were recorded. [c] In each case the reaction mixture was warmed to 90° in order to complete the reaction.

Since the Prevost reaction with silver carboxylates provides a method for obtaining either *cis*- or *trans*-α-glycols without recourse to reagents such as osmium tetroxide or performic acid attempts were made to convert the *trans*-iodoacetates into di-oxygenated derivatives. Solvolysis[6] in wet acetic acid under reflux afforded high yields of the corresponding *cis*-hydroxyacetates while solvolysis in dry acetic acid with added sodium acetate afforded the *trans*-diacetates. Moreover, the overall conversion into the *cis*-hydroxyacetates could be effected from the original alkene without isolation of the α-iodocarboxylate.

Hitherto, the only synthetic transformation employing thallium(I) carboxylates and molecular halogen has been the Hunsdiecker reaction in which treatment of a carboxylate with bromine in carbon tetrachloride results in bromodecarboxylation to give alkyl bromides in high yields.[7] The use of thallium(I) carboxylates for the formation of α-iodocarboxylates and their solvolysis products, extends the use of thallium(I) salts and the versatility of thallium in organic synthesis.[8]

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