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Synthesis of 4-halomercury crotonates

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Abstract

4-Halomercury crotonates have been synthesized in high yield by reaction of carboalkoxyalkylidene-triphenylphosphoranes with α-halomercury acetaldehydes.

Introduction

The preparation of olefins by reaction of alkylidene-triphenylphosphoranes with aldehydes and ketones, the Wittig reaction [1], is a very important procedure in organic synthesis [2–5], but no reactions of Wittig reagents with α-metallo-carbonyl compounds have been reported to date. We describe here the results of a study of the reaction between carbalkoxyalkylidene-triphenylphosphoranes and α-halomercury acetaldehydes, to give 4-halomercury crotonates.

Results and discussion

The 4-halomercury crotonates were prepared by the reaction illustrated in eq. 1.

$$\underset{(1)}{XHgCH_2CHO} + \underset{(2)}{Ph_3P{=}C(R^1)COOR^2} \rightarrow \underset{(3)}{XHgCH_2CH{=}C(R^1)COOR^2} + Ph_3PO \quad (1)$$

Compound **1** exists essentially in the ketonic form, no keto-enol equilibrium being detectable [6]. Because of the interaction between the mercury atom and the carbonyl group, the carbon–mercury bond is rather labile and is readily attacked by bases and acids [6]. For this reason the choice of reactants was restricted to stabilized Wittig reagents such as carbalkoxyalkylidene-triphenylphosphoranes **2**. These reagents could be obtained in crystalline form. In apolar aprotic solvents they are only slightly basic, nucleophilic species. A solution of the reagents **1** and **2** in benzene was refluxed under dry nitrogen for 3 h. The resulting 4-halomercury

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Table 1

Yields, melting points, and mass spectral data for compounds **3a**–**3f**

Product	Yield (%)	M.p. (°C)	Mass (obs./calc.)
$ClHgCH_2CH=CHCOOCH_3$ (**3a**)	88	133	334/335
$BrHgCH_2CH=CHCOOCH_3$ (**3b**)	86	143	379/379
$ClHgCH_2CH=CHCOOCH_2CH_3$ (**3c**)	86	83	348/349
$BrHgCH_2CH=CHCOOCH_2CH_3$ (**3d**)	87	85	393/393
$ClHgCH_2CH=C(CH_3)COOCH_2CH_3$ (**3e**)	86	115	362/363
$BrHgCH_2CH=CCH_3COOCH_2CH_3$ (**3f**)	88	145	–

crotonates **3** were purified by recrystallization from ethanol. The results are summarized in Table 1.

The method provides an efficient route to 4-metallo-(*E*)-crotonates **3** from readily available starting materials. The compounds **3** may be useful for further syntheses.

Experimental

Infrared spectra were recorded on a Perkin–Elmer 177 spectrophotometer and ^1H NMR spectra on a Bruker WP 80 SY spectrometer at 80 MHz in $CDCl_3$ (TMS internal), and mass spectra were obtained with a Nermag RC10-10C GC/MS system. Solvents were dried by standard procedures and stored under nitrogen.

General procedure for the preparation of 4-halomercury crotonates 3

A stirred solution of α-halomercury acetaldehyde **1** (0.01 mol) and carbalkoxyalkylidenetriphenylphosphorane **2** (0.01 mol) in 100 ml of dry benzene under dry nitrogen was kept under reflux for 3 h, then cooled to room temperature and filtered to remove traces of mercury. The filtrate was concentrated to dryness in vacuo. The residue was washed with ethanol (10 ml) to remove triphenylphosphine oxide, and subsequently recrystallized from 30 ml of ethanol to give the white crystalline products **3a**–**3f** in 86–88% yield.

The IR spectra of the 4-halomercury crotonates exhibit strong bands indicative of the C=C group at 1620–1630 cm^{-1} and the C=O group at 1680–1720 cm^{-1}. Yields, melting points, and mass spectral data are given in Table 1; complete ^1H NMR data for **3a**–**3f** are given below.

(*E*)-Methyl-4-chloromercurio-but-2-enoate; $ClHgC(H^a)_2CH^b=CH^cCOOC(H^d)_3$ (**3a**). 2.88 (dd, J_{ab} 10.0 Hz, J_{ac} 1.0 Hz, J(Hg, H) 154.3 Hz; $2H^a$), 3.60 (s; $3H^d$), 5.85 (dt, J_{bc} 15.2 Hz; H^c), 7.14 (dt; H^b).

(*E*)-Methyl-4-bromomercurio-but-2-enoate; $BrHgC(H^a)_2CH^b=CH^cCOOC(H^d)_3$ (**3b**). 2.87 (dd, J_{ab} 10.2 Hz, J_{ac} 1.0 Hz, J(Hg, H) 160.0 Hz; $2H^a$), 3.63 (s; $3H^d$), 5.87 (dt, J_{bc} 15.3 Hz; H^c), 7.14 (dt; H^b).

(*E*)-Ethyl-4-chloromercurio-but-2-enoate; $\mathrm{ClHgC(H^a)_2CH^b{=}CH^cCOOC(H^d)_2\text{-}C(H^e)_3}$ (**3c**). 1.22 (t, J_{de} 7.4 Hz; 3$\mathrm{H^e}$), 2.72 (dd, J_{ab} 9.0 Hz, J_{ac} 1.0 Hz, J(Hg, H) 153.0 Hz; 2$\mathrm{H^a}$), 4.15 (q; 2$\mathrm{H^d}$), 5.85 (dt, J_{bc} 15.0 Hz; $\mathrm{H^c}$), 7.12 (dt; $\mathrm{H^b}$).

(*E*)-Ethyl-4-bromomercurio-but-2-enoate; $\mathrm{BrHgC(H^a)_2CH^b{=}CH^cCOOC(H^d)_2\text{-}C(H^e)_3}$ (**3d**). 1.22 (t, J_{de} 7.2 Hz; 3$\mathrm{H^e}$), 2.73 (dd, J_{ab} 8.2 Hz, J_{ac} 0.5 Hz, J(Hg, H) 152.0 Hz; 2$\mathrm{H^a}$), 4.06 (q; 2$\mathrm{H^d}$), 5.66 (t, J_{bc} 15.2 Hz; $\mathrm{H^c}$), 7.10 (dt; $\mathrm{H^b}$).

(*E*)-Ethyl-4-chloromercurio-2-methylbut-2-enoate; $\mathrm{ClHgC(H^a)_2CH^b{=}CC(H^c)_3\text{-}COOC(H^d)_2C(H^e)_3}$ (**3e**). 1.29 (t, J_{de} 7.10 Hz; 3$\mathrm{H^e}$), 1.92 (br.s; 3$\mathrm{H^c}$), 2.68 (d, J_{ab} 9.3 Hz, J(Hg, H) 147 Hz; 2$\mathrm{H^a}$), 4.24 (q; 2$\mathrm{H^d}$), 7.04 (t; $\mathrm{H^b}$).

(*E*)-Ethyl-4-bromomercurio-2-methylbut-2-enoate; $\mathrm{BrHgC(H^a)_2CH^b{=}CC(H^c)_3\text{-}COOC(H^d)_2C(H^e)_3}$ (**3f**). 1.23 (t, $J_{de} = 7.10$ Hz; 3$\mathrm{H^e}$), 1.90 (br.s; 3$\mathrm{H^c}$), 2.71 (d, J_{ab} 9.5 Hz, J(Hg, H) 154 Hz; 2$\mathrm{H^a}$), 4.25 (q; 2$\mathrm{H^d}$), 7.14 (t; $\mathrm{H^b}$).

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