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Preliminary Communication

Selectivity of mercury(II) salts in reactions with α,β-unsaturated stannyl esters

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Abstract

Demetallation reactions of tri-n-butyltin carboxylates of some α,β-unsaturated carboxylic acids (acrylic, crotonic, cinnamic, sorbic and cyclohexylidene acetic) with mercury(II) salts (HgX_2; X = Cl, OAc) occurred selectively, and no mercuration of the olefinic double bond was detected.

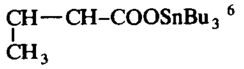
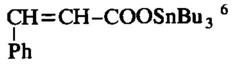
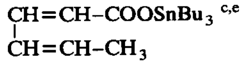
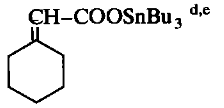
1. Introduction

The mercuration of olefins (isolated/conjugated) with mercury(II) salts is a well documented reaction [1]. The resulting organomercurials have found many applications in organic synthesis [2]. For example, the preparation of serin [3] involves the solvomercuration of the carbon–carbon double bond of methyl acrylate upon treatment with mercuric acetate in methanol, whereas organotin carboxylates undergo demetallation with mercury(II) salts as reported by Roy *et. al* [4]. With these observations in mind, it is of interest to investigate the reactions between α,β-unsaturated stannyl carboxylates and mercury salts. We report here the difference in reactivity towards mercury(II) salts observed in the case of stannyl esters and their alkyl esters, and we believe that this portends certain potential in organic synthesis.

2. Results and discussion

Our investigation embodied several types of α,β-unsaturated tin carboxylates of unsubstituted (acrylic), β-monosubstituted (crotonic, cinnamic and hexa-2,4-dienoic) and β,β-disubstituted (cyclohexylidene acetic) carboxylic acids. The reactions of these esters with

TABLE 1.

Entry	Tin carboxylates	HgX_2	Solvent	Time/Temp.	Yield [a] of BuHgCl (%)	Yield [a] of Acid (%).
1	$CH_2{=}CH\text{-}COOSnBu_3$ [b]	X = Cl	MeOH	48 h/r.t.	89	42
		X = Cl	CH_3CN	6 h/reflux	86	40
		X = OAc	MeOH	48 h/r.t.	84	30
		X = OAc	CH_3CN	6 h/reflux	82	42
2	 $\underset{CH_3}{CH}\text{—}CH\text{-}COOSnBu_3$ [6]	X = Cl	MeOH	48 h/r.t.	40	45
		X = Cl	PhH	4 h/reflux	88	43
		X = OAc	CH_3CN	4 h/reflux	96	47
		X = OAc	PhH	4 h/reflux	84	48
3	 $\underset{Ph}{CH}{=}CH\text{-}COOSnBu_3$ [6]	X = Cl	MeOH	48 h/r.t.	96	45
		X = Cl	CH_3CN	6 h/reflux	94	48
		X = OAC	MeOH	48 h/r.t.	85	46
		X = OAC	CH_3CN	6 h/reflux	90	49
4	 $\underset{CH=CH\text{-}CH_3}{CH}{=}CH\text{-}COOSnBu_3$ [c,e]	X = OAc	MeOH	48 h/r.t.	71	50
		X = Cl	PhH	4 h/reflux	76	43
		X = Cl	CH_3CN	6 h/reflux	92	59
5	 [d,e]	X = OAc	MeOH	48 h/r.t.	73	48
		X = Cl	PhH	4 h/reflux	78	44

[a] Yield of isolated pure product. [b] M.p. 69–70°C (Lit. [8] 69–70°C). [c] M.p. 84–85°C. [d] M.p. 80°C. [e] Compounds listed in entries 1, 4 and 5 gave satisfactory ^{1}H-NMR spectral data.

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mercuric chloride and mercuric acetate were studied in different solvents ranging from protic/aprotic polar to aprotic nonpolar (Table 1). In each case, butyl mercuric chloride and the corresponding acids were obtained after hydrolysis in fair to excellent yields. The formation of butyl mercuric chloride in the case of using mercuric acetate probably occurred [5] during washing of the reaction mixture with brine. Although change in the solvents did not significantly affect the yields of the products, the use of methanol, however, required a lower temperature. The results are summarised in Table 1.

While the alkyl esters of α,β-unsaturated acids, upon treatment with mercury(II) salts, undergo solvomercuration of carbon–carbon double bonds [2,3], the corresponding stannyl esters, upon similar treatment, react preferentially at the ester function keeping the olefin unreacted. Thus, by using the stannyl esters we were able to protect the carbon–carbon double bond and thereby provide a useful approach for preferential reactions of different functionalities in α,β-unsaturated esters towards mercury(II) salts. This method also provides a mild and neutral condition for hydrolysis of alkyl or aryl esters [6].

3. Experimental details

General procedure

To a solution of tri-n-butylstannyl carboxylates (2 mmol) in a solvent (10 ml) were added mercury(II) salt (2 mmol) (HgX_2; X = Cl, OAc) and the mixture was stirred under the conditions noted in Table 1. A small amount of white solids precepitated during the reaction which were filtered off. The filtrate was diluted with ether, and the organic layer was then washed with aqueous sodium chloride and dried over anhydrous Na_2SO_4. Evaporation of volatiles afforded the residue, which was crystallized from light petroleum to give BuHgCl as shining flakes in excellent yields.

M.p. 128°C (lit. [7] 127–130°C). ^{1}H-NMR (270 MHz, $CDCl_3$, ppm): δ 2.1 (t, 2H, $J = 7.13$ Hz), 1.78–1.67 (m, 2H), 1.48–1.34 (m, 2H), 0.95 (t, 3H, $J = 7.29$ Hz). ^{13}C-NMR (22.40 MHz, $CDCl_3$, ppm for APT spectra a (+) indicates 0 or 2 attached protons and a (−) indicates 1 or 3 attached protons): δ 33.06 (+), 30.09 (+), 27.81 (+), 13.47 (−). Anal. Found: C, 16.08; H, 3.17. C_4H_9HgCl calcd.: C, 16.38; H, 3.07%.

The mother liquor was diluted with ether and washed with saturated aqueous sodium bicarbonate. The aqueous phase was made acidic (3 N HCl) and extracted with ether. The organic phase was washed with aqueous sodium chloride, dried (Na_2SO_4) and evaporated to afford the corresponding acids, then recrystallized from benzene–light petroleum. Physical and spectral data of all acids isolated are identical with those of authentic samples.

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