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SHORT PAPER

Facile esterification promoted by the triphenylstibine oxide–phosphorus sulfide (Ph_3SbO/P_4S_{10}) system

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Various esters are conveniently prepared by direct esterification of the corresponding carboxylic acids with alcohols catalyzed by a triphenylstibine oxide–phosphorus(V) sulfide combined system (Ph_3SbO/P_4S_{10}) under mild conditions (25–80 °C).

Keywords: Triphenylstibine oxide, organoantimony, phosphorus(V) sulfide, carboxylic acids, esterification of carboxylic acids, catalyst for esterification

INTRODUCTION

Although a large number of acylating agents such as acyl halides, anhydrides and active esters, etc., accessible to the preparation of esters have been extensively developed, direct esterification via alkoxy-dehydroxylation of carboxylic acids with alcohols is still attractive in organic synthesis involving industrial aspects with respect to its simple and straightforward manner.[1,2] In this paper we describe the introduction of a new, facile and effective catalyst for such a straightforward esterification, consisting of triphenylstibine oxide and phosphorus(V) sulfide.

RESULTS AND DISCUSSION

Thiocarboxylic acids (Fig. 1, **4**) in general possess high acylating power towards amines, leading to facile preparation of amides[3–5] but they display low reactivity to alcohols, which perhaps results from a lower basicity of alcohols than amines. For example, the reaction of thioacetic acid with butylamine gave *N*-butylacetamide in quantitative yield at 20 °C for 1 h,[5] while the reaction of thioacetic acid with butanol gave butyl acetate in only 7% yield at 70 °C for 24 h. In contrast, the reaction of acetic acid with butanol in the presence of catalytic amounts of Ph_3SbO/P_4S_{10} proceeded to give butyl acetate in 91% yield even at 25 °C for 5 h. However, neither of the components of the catalyst system separately promoted the esterification at 60 °C as shown in Table 1. Meahwhile this catalyst system is also known to convert carboxylic acids into compound **4** conveniently.[6] We presumed that Ph_3SbO also accelerates the acylation of alcohols with **4** thus formed *in situ* (Eqns [2] and [3]) and we attempted to prepare several esters (**3**) from carboxylic acids (**1**) and alcohols (**2**) by the catalysis of Ph_2SbO/P_4S_{10}. Typical results obtained are summarized in Table 1.

Simple aliphatic and aromatic esters could be readily prepared in good yields under similar mild conditions, e.g. 25 and 50 °C. respectively, without the formation of dithio-esters. Here it should be remembered that the formation of trialkyl tetrathiophosphates (**5**) or Lawesson's type phosphorus–sulfur reagents (**6**) that have potential thionation abilities is known to be an essential

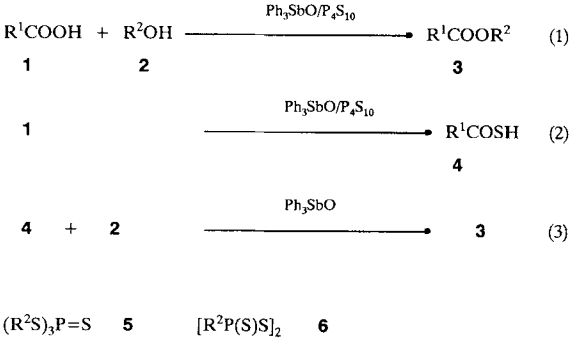

Figure 1

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function of the involvement of P_4S_{10} toward alcohols at higher temperatures than 100 °C.[7–9] Thus the reaction of **1** with **2** promoted by P_4S_{10} generally gives dithio-esters under these conditions.[7,8] In contrast, no dithio-ester is obtained in our runs because of low reaction temperatures. Consequently these results support the above mentioned route (Eqns [2], [3]).

Slightly more severe conditions, e.g. a temperature such as 80 °C and prolonged periods such as 24 h, were required for the synthesis of pivalic esters. In these runs the formation of **5**, which was detected with GC MS analysis, perhaps caused the low yield of t-butyl pivalate. The catalyst system could also produce ethyl dichloroacetate, ethyl glycolate and t-butyl acrylate in good yields, ignoring the interference from several labile substituents such as chloride, hydroxyl and the carbon–carbon double bond. Further, it should be emphasized that esterification of *N*-protected glycine proceeded readily and the corresponding ester of the amino acids was obtained in 90% yield. Additionally, adipic acid is effectively converted into its diester.

Although a few catalysts such as tertiary phosphine bromides[10] and phosphonium salts,[11] organotin compounds,[12–15] cesium salts[16] and Lewis acids such as BF_3 etherate[17] have been claimed to have catalytic activities in esterification, they are operative practically only at higher reaction temperatures, in high concentrations sometimes exceeding equimolar amounts, and/or within relatively few compounds for esterification. In contrast, the new catalyst system Ph_3SbO/P_4S_{10} can overcome these limitations. Accordingly, it should be emphasized again that the catalytic activity of Ph_3SbO/P_4S_{10} is thought to be superior to those catalyst systems already reported.

EXPERIMENTAL

Boiling and melting points are uncorrected. ^1H NMR, ^{13}C NMR and IR spectra (KRS-5 windows or KBr pellets) were recorded with a Hitachi R 90H FT spectrometer and a Hitachi 260-30 spectrophotometer, respectively. MS were obtained using a JEOL JMS-DX303 (Facualty of Engineering, Osaka University). Triphenylstibine oxide (Ph_3SbO) was prepared by hydrogen peroxide (H_2O_2) oxidation of triphenylstibine (Sankyo Synthetic Chemicals Co. Ltd, Tokyo) at −20 °C for 20 h.[3] Tetraphosphorus decasulfide (P_4S_{10}) (Wako, exta pure grade) was purified further by Soxhlet extraction with carbon disulfide (CS_2).[3] Other carboxylic acids and alcohols were used after distillation or recrystallization. All spectra and analysis data were consistent with the assigned structures.

General procedure for the catalytic esterification by the Ph_3SbO/P_4S_{10} system

To a solution of 50 mmol of the corresponding carboxylic acids (**1**) in 30 cm^3 (*ca* 0.5 mol) of alcohols (**2**) were added 2.5 mmol (0.92 g) of

Table 1 Catalytic esterification by Ph_3SbO/P_4S_{10}

R^1	R^2	*T* (°C)	*t* (h)	Yield (%)[a]	B.p. (°C)[lit.]
Me	n-Bu	25	5	91	125 [125][18]
		60	12	21[b]	
		60	12	25[c]	
Cl_2CH	Et	25	5	83	50–55/10 Torr
$HOCH_2$	Et	25	5	81	56/20 Torr
Et	Ph	25	6	70	210 [211][19]
CH_2=CH	t-Bu	25	5	67	60/50 Torr [61/60 Torr][20]
t-Bu	t-Bu	80	24	10[d]	135 [135][21]
t-Bu	$(CH_2)_5CH_3$	80	24	69	85/15 Torr
$HOOC(CH_4)/EtOOC(CH_2)_4$	Et	25	5	85	65/0.5 Torr
Ph	n-Bu	50	24	89	148/60 Torr [248][22]
Ph	Ph	50	24	55	70[e] [69–70][23]
$PhCH_2OOCNHCH_2$	Et	25	5	90	35–35.5[e] [35.5–36.5][24]

[a] Isolated yields with respect to **1** used. [b] Ph_3SbO was absent. [c] P_4S_{10} was absent. [d] The formation of the corresponding **5** was detected by GC MS analysis. [e] Melting points (°C).

Ph_3SbO and 5 mmol (2.22 g) of P_4S_{10}. After the reaction was completed, the residual solid, mainly consisting of the unreacted catalyst, was removed by filtration. Careful evaporation of the excess alcohols resulted in colorless oils. Pure esters were separated by Kugelrohr distillation.

Ethyl dichloroacetate

Analysis: Calcd for $C_4H_6Cl_2O_2$: C, 30.60; H, 3.85; Cl 45.16. Found: C, 30.50; H, 3.66; Cl, 45.36%. MS (CI, isobutane): *m/z* (%) 157 (100) [$M^+ + H$, $^{35}Cl_2$]. IR (KRS-5): ν 1742 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 5.87 (1H, s, Cl_2CH), 4.23 (2H, q, $J = 7.15$ Hz, CH_2), 1.24 (3H, s, CH_3). ^{13}C NMR ($CDCl_3$): δ 164.2 (s, CO), 64.2 (d, Cl_2CH), 63.5 (t, CH_2), 13.6 (q, CH_3).

Ethyl hydroxyacetate

HR MS: Calcd for $C_4H_8O_3$: 104.0473. Found: 104.0499. IR (KRS-5): ν 1738 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 4.11 (2H, q, CH_2O), 4.06 (2H, s, CH_2OH), 3.8 (1H, br.s, OH), 1.18 (3H, t, CH_3). ^{13}C NMR ($CDCl_3$): δ 172.6 (s, CO), 60.4 (dt, $^1J_{^{13}C-^1H} = 145.8$ Hz, $^2J_{^{13}C-^1H} = 4.2$ Hz, CH_2OH), 59.9 (t, CH_2), 13.5 (q, CH_3).

n-Hexyl trimethylacetate

Analysis: Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 70.96; H, 12.16%. MS (EI): *m/z* (%) 186 (100) [M^+]. IR (KRS-5): ν 1725 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 4.18 (2H, t, $J = 6.3$ Hz, OCH_2), 1.2–1.8 (10H, m, CH_2), 1.32 (9H, s, CH_3), 1.02 (3H, t, $J = 5.0$ Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 177.7 (s, CO), 63.9 (t, OCH_2), 38.9 (s, $(CH_3)_3C$—), 31.1 (t, OCH_2CH_2), 28.3 (t, $OCH_2CH_2CH_2$), 26.8 (q, $(CH_3)_3C$), 25.3 (t, $CH_2CH_2CH_3$), 22.2 (t, CH_2CH_3), 13.5 (q, CH_3).

Diethyl adipate

HR MS: Calcd for $C_{10}H_{18}O_4$: 202.1205. Found: 202.1224. IR (KRS-5): ν 1730 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 3.97 (4H, q, $J = 7.0$ Hz, CH_3CH_2), 2.17 (4H, t, $J = 6.8$ Hz, $O_2CCH_2CH_2$), 1.51 (4H, t, CH_2), 1.10 (6H, t, CH_3). ^{13}C NMR ($CDCl_3$): δ 172.8 (s, C=O), 59.9 (t, CH_2O), 33.6 (t, CH_2CO_2), 24.2 (t, CH_2), 14.0 (q, CH_3).

Catalytic esterification of *N*-carbobenzyloxyglycine

After the reaction, crude ester was obtained as a white gum which was chromatographed on silica gel (Wako C-200, diam. 15 mm × 200 mm, elution with hexane/ethyl acetate, 1:9 v/v) to give pure ester (9.24 g, 90%).

***N*-Carbobenzyloxyglycine ethyl ester**

^{1} NMR ($CDCl_3$): δ = 7.24 (br.s, 5H, Ph), 5.0–5.3 (br., 1H, NH), 5.02 (s, 2H, $PhCH_2$), 4.10 (q, 2H, CH_2), 3.85 (d, $J = 5.7$ Hz, 2H, NCH_2CO), 1.16 (t, $J = 7.0$ Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ = 169.6 (s, CO_2), 156.0 (s, NCO_2), 135.9 (s, *ipso*), 127.9 and 127.5 (d, aromatic), 66.5 (t, CH_2, $PhCH_2$), 60.9 (t, CH_2), 42.4 (t, NCH_2CO_2), 13.8 (q, CH_3).

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