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Synthesis and Characterization of 2-Carboxyethyltriphenyl Phosphonium Tribromide and Its Application as Catalyst in Silylation of Alcohols and Thiols Under Solvent-Free Condition

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SYNTHESIS AND CHARACTERIZATION OF 2-CARBOXYETHYLTRIPHENYL PHOSPHONIUM TRIBROMIDE AND ITS APPLICATION AS CATALYST IN SILYLATION OF ALCOHOLS AND THIOLS UNDER SOLVENT-FREE CONDITION

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GRAPHICAL ABSTRACT

 $PPh_{3} + CH_{2}=CH-COOH \xrightarrow{KBr} Ph_{3}P-CH_{2}-CH-COOH \xrightarrow{\textcircled{W}} KMnO_{4} \xrightarrow{\textcircled{W}} Br_{3} \xrightarrow{\textcircled{W}} Br_{3} \xrightarrow{\textcircled{W}} Ph_{3}P-CH_{2}-CH_{2}-COOH$

Abstract A phosphonium-based catalyst, 2-carboxyethyltriphenyl phosphonium tribromide (CTPTB), has been synthesized by reacting triphenyl phosphine with acrylic acid and potassium bromide under solvent-free condition followed by oxidation of Br^- to Br_3^- with KMnO₄. This hitherto unknown tribromide reagent is characterized by ultraviolet–visible, Fourier transform–infrared, ¹H NMR, and ³¹P NMR spectroscopy. Its efficacy as catalyst is established by investigating its catalytic activity in silylation of alcohols and thiols by hexamethyl disilazane (HMDS). It is found to be a very good catalyst and selectively and efficiently catalyzes the silylation reactions.

Keywords Acrylic acid; alcohols; hexamethyl disilazane (HMDS); oxidation; potassium bromide; silylation; tribromide reagent

INTRODUCTION

The exploration of new reagents and development of green methodologies to curb environmental hazards have become challenging tasks in synthetic organic chemistry.^[1] Recent years have witnessed a large number of reports on the synthesis of various reagents/catalysts, especially organic ammonium tribromides (OATBs), and their application in organic reactions.^[2] The most frequently used quaternary ammonium tribromide reagents are tetrabutyl ammonium tribromide (TBATB),^[3] cetyltriethyl ammonium tribromide (CTETB),^[4] 1,2-dipyridinium ditribromide (DPTBE),^[5] N-methylpyrrolidine-2-one hydrotribromide (MPHT),^[6] quinoline

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hydrotribromide (QHTB),^[7] benzyltriphenyl phosphonium tribromide,^[8] tridecylmethyl phosphonium tribromide,^[9] ethyltriphenyl phosphonium tribromide,^[10] and crown ether entrapped tribromide.^[11] These are preferable as reagents/catalysts because they are highly efficient, less hazardous, easy to handle, and usually give good yields and selectivity of products. As a part of our continuous endeavour to develop new green protocols for synthesis of organic ammonium tribromides as well as biologically important compounds,^[12] we report herein the synthesis and characterization of a new tribromide compound, 2-carboxyethyltriphenyl phosphonium tribromide (CTPTB). With successful synthesis of this new reagent, it becomes imperative to study the efficiency of this compound as a catalyst in the silylation of alcohols and thiols. It may be emphasized that protection of reactive hydroxyl groups are indispensible in multistep reactions for the synthesis of polyfunctional compounds. One of the most common and easy methods for protection of hydroxyl and thiol groups is silylation by converting them into corresponding silyl ethers.^[13] The reagents that are used in the traditional and conventional processes are R₃SiCl,^[14] MeSiN=C(Me)OSiMe,^[15] Me₃SiCl, or Me₃SiOTf in the presence of base.^[16] However, many of these methods have demerits, such as lack of reactivity, long reaction times, and difficult-to-remove by-products and co-bases during the reaction.^[17] HMDS is commercially available, cheap, noncorrosive, and easy to handle for the formation of trimethyl silvl ether, which generates only ammonia gas as by-product.^[18] A variety of catalysts, such as Cu(SO₄) · 5H₂O, Al(OTf)₃, trichloroiso cyanuric acid, and I2, have been already reported efficient synthesis of silvlated products.^[18(b),19] However, no report on solvent-free silvlation using CTPTB as a catalyst has been observed. The solvent-free condition is preferrable for environmental issues and also for obtaning good yields and pure products.^[20]

RESULTS AND DISCUSSION

The present protocol is an easy and clean synthesis of 2-carboxyethyltriphenyl phosphonium tribromide under solvent-free condition. The crystalline compound is stable for several days at room temperature without decomposition. The reaction involves the nucleophilic attack of triphenyl phosphine^[21] on β -carbon of acrylic acid to generate an ylide I. In the next step, KMnO₄ serves as good oxidant^[12(a)] in the presence of sulfuric acid to convert Br⁻ to Br₃⁻. The plausible mechanism is depicted in Scheme 1.

The formation of tribromide was confirmed by electronic absorption spectroscopy and FT-IR technique (Scheme 1). An intense band at 282 nm (Fig. 1) is characteristic of tribromide anion (Br_3^{-}) .^[22] The infrared (IR) spectra of CTPTB (Fig. 2) exhibits characteristic (Br_3^{-}) bands at 44 (n_1) and 188 (n_2) cm⁻¹ for bending

Scheme 1. Reaction showing the formation of 2-carboxyethyltriphenyl phosphonium tribromide.



Figure 1. UV-vis spectra of CTPTB.

and asymmetric stretching, respectively.^[23] The tribromide gives two peaks, one singlet ($\delta = 29.18$) and one triplet ($\delta = 22.55$, 2H), in its ³¹P {¹H} NMR spectrum, which is consistent with literature information.^[24] Parish et al. found that PPh₃ shows singlet with δ values -7. However tetra-phenylphosphonium cations Ph₃PH⁺ and Ph₄P⁺ give signals at $\delta - 1$ ppm and $\delta + 21$ ppm respectively.^[25] The downfield shift (to $\delta = 23$) in the synthesized tribromide is assumed to be for the fourth acrylic acid group attached to phosphorous atom.

The silylation of ROH and RSH is investigated under solvent-free conditions by using HMDS and a catalytic amount of CTPTB (Scheme 2). A variety of compounds were chosen for this purpose (Table 1). These include aromatic, aliphatic, and alicyclic alcohols and thiols. The silylated products were characterized by comparing their melting points, FTIR, and ¹H NMR spectra with those of authentic

1.1 1.0 538.12856646.14003 Transmittance 115.72657 0.9 379.96891 0.8 0.7 0.6 189.02007 100 400 700 200 300 500 600 Wavenumber [cm⁻¹]

Figure 2. FT-IR spectra of CTPTB.

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$$\operatorname{ROH}/\operatorname{RSH}$$
 + HDMS $\xrightarrow{\operatorname{CTPTB}(\operatorname{cat.})}$ ROTMS/ RSTMS + NH₃
Silica Gel, r.t

Scheme 2. Silylation of alcohols and thiols.

Entry	Substrate ^a	Products ^b	Catalyst amount (mmol)	Time (min)	Yield ^{<i>c,d</i>} (%)	
1	ОН	отмя	0	45	65	
2	ОН	ОТМЯ	0.1	4	87	
3	ОН	отмя	0.1	10	80	
4	он	OTMS	0.1	5	81	
5	ОН	OTMS	0.1	6	90	
6	мео	OTMS	0.1	4	85	
7	ОН	ОТМЯ	0.1	7	75	
8	ОН	отмя	0.1	7	75	
9	SH	STMS	0.1	4	78	
10	SH	STMS	0	30	67	
11	SH	STMS	0.1	8	80	
12	SH	STMS	0.1	8	81	

Table 1	۱.	Silylation	of	alcohols	and	thiols	by	' using	HMDS	and	catalyti	e amount	of	CTP	ТΒ
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(Continued)

Entry	Substrate ^d	P roducts ^b	Catalyst amount	Time (min)	Yield ^{c,d}
Litti y	Substrate	Tioducts	(mmoi)	(mm)	(70)
13	SH	STMS	0.1	6	68
14	MeO	STMS	0.1	7	70

Table 1. Continued

^aAlcohol/thiols (20 mmol), HMDS (10 mmol), CTPTB (0.1 mmol).

^bProducts were identified by their IR and NMR spectral data and comparing them with published data. ^cIsolated yield.

^dReactions were monitored by TLC and products were extracted by ethyl acetate.



Scheme 3. Catalytic loop showing the plausible mechanism of silylation by CTPTB.

samples.^[26] The plausible mechanism is represented using a catalytic cycle (Scheme 3) in which the function of CTPTB and the evolution of ammonia have been depicted. It is believed that intermediate **II** reacts with ROH and/or RSH to produce Br_2 and NH₃ alongside the silylated products. The Br_2 thus produced reacts with tetraalkyl phosphonium bromide to form the CTPTB. The reactions, carried out without a catalyst, taking butanol and thiol as substrate (Table 1), also resulted in the formation of silylated products; however, such noncatalytic reactions were observed to give poor yield in relatively long reaction time.^[27]

CONCLUSION

In conclusion, a new phosphonium-based tribromide reagent, 2-carboxytriphenyl phosphonium tribromide, has been synthesized by reacting triphenyl phosphine with

acrylic acid and KBr in presence of mildly acidic $KMnO_4$ solution. The compound is found to be good and efficient catalyst for silylation of alcohols and thiols by HMDS under solvent-free condition. The method is simple, mild, nonhazardous, and less time-consuming. Although several methods are known for the protection of hydroxyl and thiol groups via silyaltion, the present methodology offers a new and useful alternative for such reactions.

EXPERIMENTAL

All the chemicals are of analytical grade and used without further purification. The completion of reaction was monitored by thin-layer chromatography (TLC). The synthesized tribromide was charaterized with UV-visible, FT-IR, and ³¹P NMR spectroscopy. The IR spectra were recorded on KBr with Magna 550 FTIR spectrometer. NMR spectra were recorded in CDCl₃ on Mercury Plus 400-MHz NMR spectrometer.

Synthesis of CTPTB

In a typical procedure, CTPTB was synthesized by mixing 2.62 g triphenyl phosphine (10 mmol) and 1 ml acrylic acid (10 mmol) in a magnetic stirrer for 10 min. To the mixture 3.57 g KBr (30 mmol) and 1.58 g of KMnO₄ (10 mmol) in 10 ml of 4 N H₂SO₄ solution were added. The whole mixture was again stirred for 10 min until an orange compound was formed. The product was extracted with ethylacetate (2 × 5 ml) and then dried in vacuum. The crude product was recrystallized to get better yield with high purity; yield 85%, mp: 138–140 °C, UV-vis: 282 nm; FT-IR: 3779, 2957, 2667, 1563, 1374, 1110, 883, 740, 188, 44 cm⁻¹; ³¹P NMR δ : 29.17, 22.8–23.2; ¹H NMR δ : 10.7 (s, 1H), 7.2–7.4 (m, 15H), 2.5 (t, 2H), 1.3 (t, 2H).

Representative Procedure for Silylation of Alcohols and Thiols

Silylation of butanol. In a representative procedure, 20 mmol of butanol was mixed with a catalytic amount of CTPTB (0.1 mmol) and a little amount of silica gel in a mortar. To the mixture, 10 mmol of hexamethyl disilazane was added drop by drop and ground well for 4 min at room temperature until the product formed. After monitoring the completion of reaction by TLC, the products were extracted with ethyl acetate (2×5 ml) and evaporated under vacuum to obtain pure butyloxytrimethylsilane. Yield: 87%; FT-IR: 2960, 2765, 1483, 1291, 1168, 1082, 948, 687 cm^{-1} ; ¹H NMR (400 MHz, CDCl₃) δ : 0.09 (s, 9H), 0.92 (t, 3H), 1.35–1.45 (m, 4H), 3.87 (m, 2H).

Silylation of thiophenol. In a representative procedure, 20 mmol of thiophenol was mixed with a catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To the mixture, 10 mmol of hexamethyl disilazane was added drop by drop and ground well for 6 min at room temperature. The completion of the reaction was monitored by TLC. After the completion, the products were extracted with ethyl acetate and evaporated under vacuum to obtain pure

phenylthiotrimethylsilane. Yield: 68%; ¹H NMR (400 MHz, CDCl₃) δ : 0.09 (s, 9H), 7.2–7.1 (m, 5H). FT-IR: 3286, 2578, 1579, 1442, 1025, 734, 689 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ : 0.09 (s, 9H), 7.2–7.1 (m, 5H).

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SUPPORTING INFORMATION

Full experimental details and data of FT-IR and ¹H NMR spectra of silylated products can be accessed on the publisher's website.

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