SUPPORTING INFORMATION

Title: *Synthesis and Characterization of 2-Carboxyethyltriphenyl Phosphonium Tribromide and its Application as Catalyst in Silylation of Alcohols and Thiols under Solvent Free Condition.*

Author(s): Rupa Rani Dey, Siddhartha Sankar Dhar

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1. Representative Procedure

Synthesis of 2-Carboxyethyltriphenyl phosphonium tribromide (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 minutes at room temperature. To the mixture, 3.57 g of KBr (30 mmol) and 1.58 g of KMnO_4 (10 mmol) in 10 ml of 4N H_2SO_4 solution were added. The whole mixture was again stirred for 10 minutes until orange colour compound was formed. The product was extracted with Et_2O (2x5 ml) and then dried in *vacuum*. The crude product was recrystallized to get better yield with high purity. Then it was preserved for further analyses. Yield-85%. Mp: 138-140°C.

Procedures for Silylation of Alcohols and Thiols

Synthesis of (Butyloxy)trimethylsilane: 2 ml of n-butanol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding butyloxytrimethylsilane (**1**, **Table 1**) in oily form. The reaction time and yield of the products are presented in Table 1.

Synthesis of (Isopropoxy)trimethylsilane: 1.5 ml of isopropanol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding isopropoxytrimethylsilane (**2**, **Table 1**). The reaction time and yield of the products are presented in Table 1.

Synthesis of (n-Octyloxy)trimethylsilane: 3.1 ml of n-octanol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding octyloxytrimethylsilane (**3, Table 1**). The reaction time and yield of the products are presented in Table 1.

Synthesis of (Benzyloxy)trimethylsilane: 2 ml of benzyl alcohol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding benzyloxytrimethylsilane (**4, Table 1**). The reaction time and yield of the products are presented in Table 1.

Synthesis of (4-Methoxybenzyloxy)trimethylsilane: 1.8 ml of 4-methoxybenzyl alcohol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding 4-methoxybenzyloxytrimethylsilane (**5, Table 1**). The reaction time and yield of the products are presented in Table 1.

Synthesis of (Cyclopentyloxy)trimethylsilane: 1.8 ml of cyclopentanol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g

of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding cyclopentyloxytrimethylsilane (**6**, **Table 1**). The reaction time and yield of the products are presented in Table 1.

Synthesis of (Cyclohexyloxy)trimethylsilane: 2 ml of cyclohexanol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding cyclohexyloxytrimethylsilane (**7**, **Table 1**). The reaction time and yield of the products are presented in Table 1.

Synthesis of (Butanethio)trimethylsilane: 2 ml of butanethiol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding butylthiotrimethylsilane (**8**, **Table 1**). The reaction time and yield of the products are presented in Table 1.

Synthesis of (Phenylthio)trimethylsilane: 2 ml of thiophenol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were

extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding phenyllthiotrimethylsilane (**9, Table 1**). The reaction time and yield of the products are presented in Table 1.

Synthesis of (4-Methylphenylthio)trimethylsilane: 2.3 ml of 4-methylthiophenol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding 4-methylphenyllthiotrimethylsilane (**10, Table 1**). The reaction time and yield of the products are presented in Table 1.

Synthesis of (Benzylthio)trimethylsilane: 2.3 ml of benzylthiol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent. Evaporation of the solvent yielded the corresponding benzylthiotrimethylsilane (**11, Table 1**). The reaction time and yield of the products are presented in Table 1.

Synthesis of (4-Methoxybenzylthio)trimethylsilane: 2.8 ml of 4-methoxybenzylthiol (20 mmol) was mixed with catalytic amount of CTPTB (0.1 mmol, 0.05 g) and a little amount of silica gel in a mortar. To it 1.61 g of hexamethyl disilazane (10 mmol) was added drop by drop and ground well for an approximate time until the product formed. The completion of reaction was monitored by TLC. After that the products were extracted with ethyl acetate (2x5 ml) and evaporated under *vacuum*. The products were further purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent.

Evaporation of the solvent yielded the corresponding 4-methoxybenzylthiotrimethylsilane (**12**, **Table 1**).

The reaction time and yield of the products are presented in Table 1.

2. UV-Vis Spectra of CTPTB

3. IR Spectra of CTPTB

3. ^{31}P NMR Spectra of CTPTB

4. IR and NMR Spectral Data of Some Selectively Chosen Products

(Butyloxy)trimethylsilane (Entry 1) IR (liquid film): 2960, 2765, 1483, 1291, 1168, 1082, 948, 687 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 0.09 (s, 9H), 0.92 (t, 3H), 1.35-1.45 (m, 4H), 3.87 (m, 2H).

(Isopropoxy)trimethylsilane (Entry 2) IR (KBr): 3116, 2959, 1721, 1660, 1577, 1413, 1054, 890, 689 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 0.10(s, 9H), 1.07 (d, J = 6.1 Hz, 6H), 3.86 (m, 1H).

(Benzyloxy)trimethylsilane (Entry 4) IR (KBr): 2958, 1615, 1493, 1286, 1116, 1008, 959, 826, 770 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 0.06 (s, 9H), 5.78 (s, 2H), 7.28 (m, 5H).

(Cyclopentyloxy)trimethylsilane (Entry 6) ^1H NMR (400 MHz, CDCl_3) δ : 0.12 (s, 9H), 1.30-1.80 (m, 8H), 4.12 (m, 1H).

(Cyclohexyloxy)trimethylsilane (Entry 7) ^1H NMR (400 MHz, CDCl_3) δ : 0.06 (s, 9H), 1.4-1.7 (m, 10H), 3.65 (m, 1H).

(Phenylthio)trimethylsilane (Entry 9) IR: 3286, 2578, 1579, 1442, 1025, 734, 689 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ : 0.09 (s, 9H), 7.2-7.1 (m, 5H).