



High Yield Synthesis of Some Aromatic Phosphonic Acid Derivatives and Related Compounds as Surface Tethers for Energy Harvesting Technologies

Amshumali Mungalimane

Department of Chemistry/Industrial Chemistry, Vijayanagara Sri Krishnadevaraya University,
Jnanasagara campus, Cantonment, Ballari-583105, **INDIA**

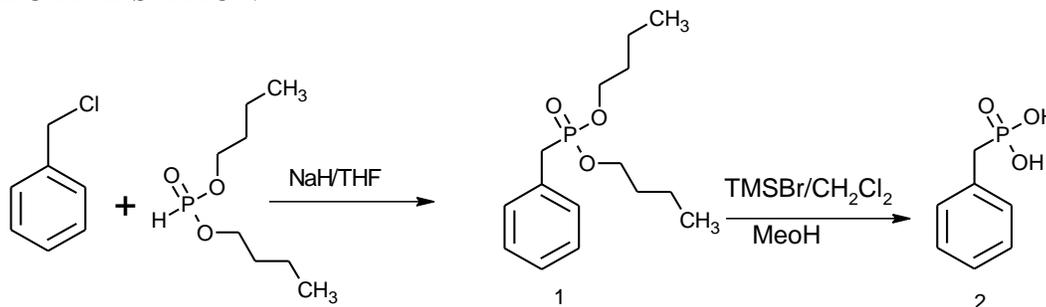
Email: amshumali@vskub.ac.in

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ABSTRACT

Efficient synthesis of novel 1-Phenyl ethyl phosphonic acid, 4-vinylbenzylphosphonic acid. Benzyl phosphonic acid and Perfluorophenyl methacrylate and such other derivatives are reported here. These derivatives have a potential application as tethers to nanoparticle surfaces that can promote efficient electron transfer process in solar energy conversion.

GRAPHICAL ABSTRACT:



Keywords: Surface tethers, Coupling reaction, Phosphonic acid derivatives, perfluorophenyl methacrylate, Solar energy conversion

INTRODUCTION

The quest for efficient solar energy conversion to produce electricity or chemical fuels has expanded significantly in the last decade [1-7]. As pointed out in these literatures, it is widely recognized that many of the key limitations to new energy conversion technology results from a lack of nanometer scale control of material composition and properties, linked with a clear understanding of how these properties impact on energy conversion efficiency.

The key steps in solar energy conversion, and solar photochemical formation of fuels, using small molecule, polymer and semiconductor nanoparticle (SC-NP) composites are recognized to be (i) light

absorption, (ii) excited state or exciting dissociation, (iii) charge separation, (iv) Charge transport and (v) charge collection (electronic) or electrochemical fuel production.

Limitations in any one of these steps translates to poor energy conversion efficiency for the entire system [8, 9]. The recent efforts in avoiding the limitations to the above steps consists of electro deposition of an ultra thin film polymer host on an activated indium tin oxide (ITO) surface providing a selective (electron blocking) back contact, and CdSe nanoparticles capped with electroactive ligands are attached electrochemically in the near surface region of the polymer film [10-12]. This provides for the direct wiring of the SC-NP to the transparent bottom contact and appears to provide a route for optimizing the use of such nanoparticles as the photoactive layer in both photo electrochemical and photovoltaic energy conversion technologies. Notable recent studies using functional ligand capping of SC-NPs have been directed towards enhancing the compatibility of the nanoparticle with polyphenylenevinylene (e.g. MEH-PPV) or polythiophene matrices [13-18], where the surface functional groups may be the trioctylphosphine oxide (TOPO) derivatives or phosphonates.

Our research work is centered about synthesizing such phosphonic acid derivatives (ligands) and testing their efficiency as adherers for efficient energy conversion. Previously we have published the series of such phosphonic acid derivatives of aliphatic hydrocarbons.[19] In continuation of this work we also prepared some interesting phosphonic acid derivatives with aromatic hydrocarbons. Therefore here we are reporting the library of such ITO tethering compounds, namely, 1-Phenyl ethyl phosphonic acid, 4-vinylbenzylphosphonic acid, Benzylphosphonic acid and Perfluorophenyl methacrylate. They have been prepared and characterized along with its intermediates. We hypothesize that these ligands would passivate the surfaces of metal chalcogenide nanoparticles and make them amenable to inclusion in a variety of polymeric hosts and/or provide for attachment at the termini of the conducting polymeric chains.

MATERIALS AND METHODS

General methods: All reactions are carried out under argon atmosphere using standard Schlenk technique, except where otherwise indicated. All glassware are previously dried in oven at 120°C and cooled to room temperature. Methacraloyl chlorides, 4-Vinyl benzyl chloride, Pentafluorophenol, Triethylamine, triethylphosphite, Trimethyl silyl bromide were used as received from Aldrich or elsewhere. NMR experiments were carried out in Bruker AM 250 in the solvent indicated in each case at 250 and 62.5 MHz for ¹H and ¹³C NMR, respectively. Chemical shifts were noted in parts per million and J values are given in hertz. Microanalyses were carried out at Indian Institute of Science, Bangalore, on LECO-CHNS analyzer, and were in a good agreement with the calculated values. High resolution mass spectrometry (HRMS) was recorded on FAB Shimadzu Instruments.

Synthesis of dibutyl benzyl phosphonate (1): In a three neck flask fitted with a reflux condenser and the argon inlet was placed sodium hydride (0.18 gm, 7.9 mmol) and 40 mL of dry THF. The mixture was stirred and dibutyl phosphate (1.53g, 7.9 mmol) was added, the mixture was stirred for 45 min with about 40 °C temperatures, the evolution of hydrogen was observed. To this solution, benzyl chloride (1g, 7.6 mmol) was added and the reaction mixture was refluxed for 18h, then the reaction mixture was allowed to cool to room temperature, evaporated the THF under vacuum, washed with water and extracted with diethyl ether. The product in diethyl ether was dried with MgSO₄ and solvent removed under vacuum gives oily liquid yield 1.45g, (5.0mmol 65%).

¹H NMR (CDCl₃, δ ppm) 0.908 (t, 6H, ³J= 7.25, CH₃) 1.33 (q, 4H, ³J=7.25, CH₂) 1.58 (q, 4H, ³J=7.00, CH₂) 3.10 (d, 2H, ²J_{PH}=21.5 Benzylic CH₂) 3.91(q, 4H, ³J=6.75, OCH₂)

Synthesis of benzyl phosphonic acid (2): Benzyl dibutyl phosphonate (1g, 3.4 mmol) was placed in a Schlenk flask fitted with Argon line, equipped with a stir bar with 10 mL of dichloromethane, followed by Bromotrimethylsilane (1.1 g, 6.9 mmol) and stirred for 24h. Stir more for 1h at 50°C temperature. After the

reaction the solvent and excess of TMSBr was removed under vacuum and 10 mL of methanol was added stirred for 1h. Methanol was removed, the off white solid was obtained yield 0.6g, (3.0 mmol, 85%)

^1H NMR (DMSO d_6 , ppm) 2.95 (m, 2H, $^2J=7.75$ CH₂) 7.26 (d of d, 5H, $^3J_1=^3J_2=10.75$, and 7.75 C₆H₅) 9.00 (broad, OH); ^{13}C NMR (DMSO d_6 , ppm) 36.46 (Benzylic CH₂) 125.90 (C-quaternary) 128.02, 129.71, 134.92 (C, aromatic)

Synthesis of dibutyl 4-vinylbenzylphosphonate (3): In a three neck flask fitted with a reflux condenser and the argon inlet was placed sodium hydride (0.18 g, 7.9 mmol) and 40 mL of dry THF. The mixture was stirred and dibutyl phosphate (1.53g, 7.9 mmol) was added, the mixture was stirred for 45 min with about 40° C temperature the evolution of hydrogen was observed. To this solution, 4-vinyl benzyl chloride (1.1 g, 7.6 mmol) was added and the reaction mixture was refluxed for 18h .then the reaction mixture was allowed to cool to room temperature, evaporated the THF under vacuums, washed with water and extracted with diethyl ether. The product in diethyl ether was dried with MgSO₄ and solvent removed under vacuum gives oily liquid yield 1.1g, (5.0 mmol 60%)

^1H NMR (CDCl₃, δ ppm) 0.908 (t, 6H, $^3J=7.25$, CH₃) 1.28 (q, 4H, $^3J=7.0$ CH₂) 1.58 (q, 4H, $^3J=7.25$ CH₂) 3.06 (d, 2H, $^2J_{\text{PH}}=21.75$ Benzylic CH₂) 3.92(q, 4H, $J=6.75$ OCH₂) 5.16 (d, 1H $^1J_{\text{CH}}=10.75$ CH₂) 5.68 (d, 1H $^1J_{\text{CH}}=17.75$ CH₂) 6.67 (dd, 1H, $^3J_{\text{CH}}=10.75$ CH) 7.19 (dd, 2H $^2J=6.25$ *Ortho* H) 7.30 (dd, 2H $^2J=11.0$ *para* H).

Synthesis of 4-vinylbenzylphosphonic acid (4): Dibutyl 4-vinylbenzylphosphonate (0.8g, 2.58 mmol) was placed in a Schlenk flask fitted with Argon line, equipped with a stir bar with 10 mL of dichloro methane. Followed by Bromo trimethyl silane (0.78 g, 5.2 mmol) and stirred for 24h. And stirred 1h with a temperature of 50° C. after the reaction the solvent and excess of TMSBr was removed under vacuum and 10 mL of methanol was added stirred for 1h. Methanol was removed the off white solid was obtained this solid was further purified by re crystallizing in hexane, almost white solid was obtained. Yield 0.4g, (2.1 mmol, 72%)

^1H NMR (DMSO d_6 , ppm) 2.99 (d, 2H, $^2J=21.25$ CH₂ benzylic) 5.22 (d, 1H, $^3J_{\text{CH}}=11.0$ CH₂) 5.81 (d, 1H, $^3J_{\text{CH}}=18.0$, CH₂) 6.71(m, 1H, $^3J_{\text{CH}}=6.5$ CH) 7.23 (d, 2H, *Ortho* H) 7.92 (d, 2H, *Para* H) 8.2(broad, -OH); ^{13}C NMR (DMSO d_6 , ppm) 112.05 (=CH₂) 124.36 (d, *ortho* C) 128.53 (d *meta* C) 133.44 (quaternary C on benzene) 135.03 (HC=).

Synthesis of dibutyl 1-phenyl ethyl phosphonate (5): In a three neck flask fitted with a reflux condenser and the argon inlet was placed sodium hydride (0.26 gm, 10.8 mmol) and 40 mL of dry THF. The mixture was stirred and dibutyl phosphate (1.5g, 7.9 mmol) was added, the mixture was stirred for 45 min with about 40 °C temperatures. The evolution of hydrogen was observed. To this solution, ethyl bromo benzene (1g, 5.4 mmol) was added and the reaction mixture was refluxed for 18h .then the reaction mixture was allowed to cool to room temperature, evaporated the THF under vacuum, washed with water and extracted with diethyl ether. The product in diethyl ether was dried with MgSO₄ and solvent removed under vacuum gives oily liquid yield 1.45g, (5.0 mmol 65%)

^1H NMR (cdcl₃, ppm) 0.822(t, 6H, CH₃) 1, 20(q, 4H, CH₂) 1.48(q, 4H, CH₂) 1.98 (t, CH₃, 3H) 3.23(q, CH 1H) 4.0 (q, 4H OCH₂)

Synthesis of 1-phenyl ethyl phosphonic acid (6): Dibutyl 1-phenyl ethyl phosphonate (1g, 3.6 mmol) was placed in a Schlenk flask fitted with Argon line, equipped with a stir bar with 10 mL of dichloromethane followed by Bromotrimethylsilane (1.1 g, 6.9 mmol) and stirred for 24h. After the reaction, the solvent and excess of TMSBr was removed under vacuum and 10 mL of methanol was added stirred for 1h. Methanol was removed, the off white solid was obtained yield 0.6g, (3.0 mmol, 85%).

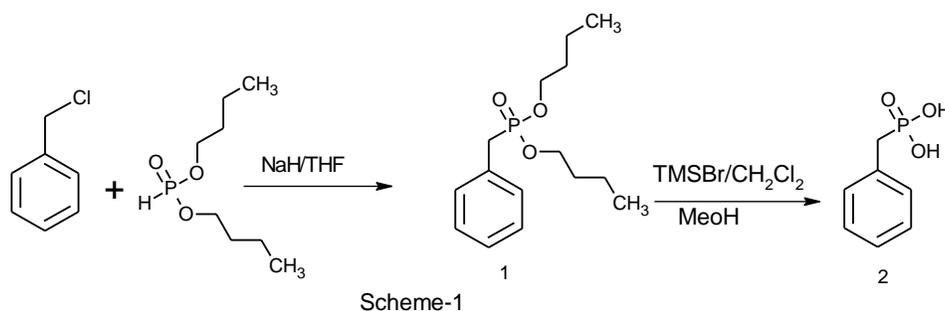
^1H NMR: 1.5 (d of d, 3H, CH_3 $J=19$ Hz) 3.31 (d of d, $J=23.5$ Hz, 1H, CH) 7.23 (broad 5H, aromatic). 9.5(s, 2H, OH); ^{13}C NMR: 14.686 (CH_3) 36.27(CH) 127.13(aromatic, para C) 128.36(aromatic ortho C,) 128.66 (aromatic, meta c) 137.01(quaternary, aromatic C)

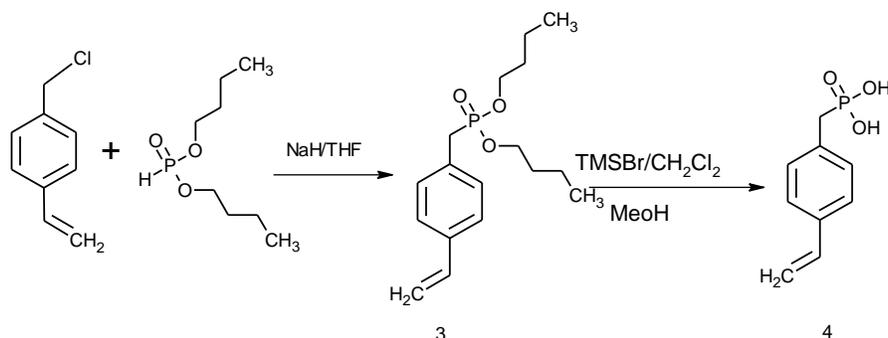
Synthesis of Perfluorophenyl methacrylate (7): Pentafluorophenol (1g, 5.4mmol) was placed in a 50 mL Schlenk flask with a stir bar fitted with argon line and the rubber septum. 25 mL of dry THF was added with stirring followed by a methacraloyl chloride (0.6g, 5.8mmol) and the mixture was cooled to 0°C . Then TEA was added (0.7g, 6.0mmol) drop wise via syringe. White precipitate was observed instantaneously. The mixture was then allowed to warm to room temperature and continued to stir for 24h. Then the THF was removed under vacuum and the mixture was washed with water and extracted 3 times with diethyl ether. Dried with MgSO_4 filtered, and solvent was removed under vacuum. The crude product was subjected to column chromatography with 50:1 Hexane: ethyl acetate. Yield 1.2g (4.8 mmol, 88%)

^1H NMR (CDCl_3 , δ ppm) 2.086 (s, 3H, CH_3) 5.910 (s, 1H, CH) 6.4 (s, 1H, CH); ^{19}F NMR (CDCl_3 , δ ppm) -153.3(t, 2F, *ortho* F) -159.0(t, 1F *para* F) -163.1(q, 2F, *meta* F); ^{13}C NMR (CDCl_3 , ppm): 18.670 (CH_3) 130.406 (CH_2) 134.287 (-C) 163.618 (C=O) 143.792 (broad, aromatic C) 140.304 (broad, aromatic C) 136.432 (broad, aromatic C)

RESULTS AND DISCUSSION

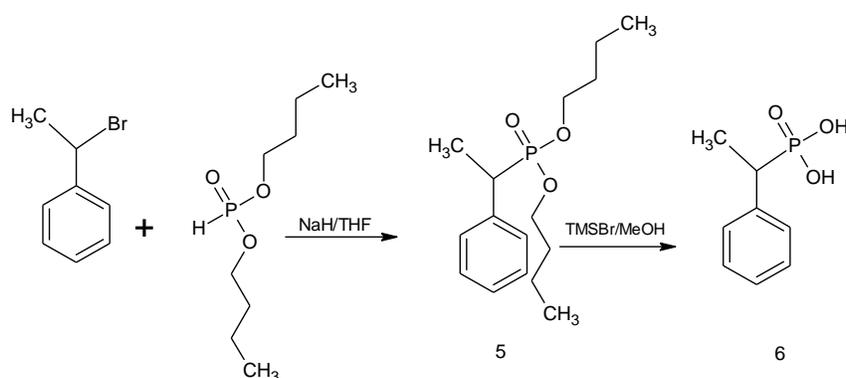
The compounds selected for synthesis is based on their suitability as ITO SC-NP tetherers and the simplicity in their synthesis. Thus for synthesizing the benzyl phosphonic acid (2) benzyl chloride and dibutyl phosphate were allowed to react in presence of sodium hydride in the solvent THF resulting in phenyl dibutyl phosphate(1) this intermediate on treating with trimethyl silyl bromide in methanolic media, resulted in the desired compound with the high yield. The overall reaction is as shown in the scheme- 1. The advantage of this type of reaction is we can synthesize the number of substituted benzyl phosphonic acids just by choosing the substituted benzyl chloride. For example in the similar method of synthesis for synthesizing the 4-vinyl benzyl phosphonic acid (4), we have taken a vinyl substituted benzyl chloride and the reaction proceeded with almost quantitative yield as shown in the Scheme-2.





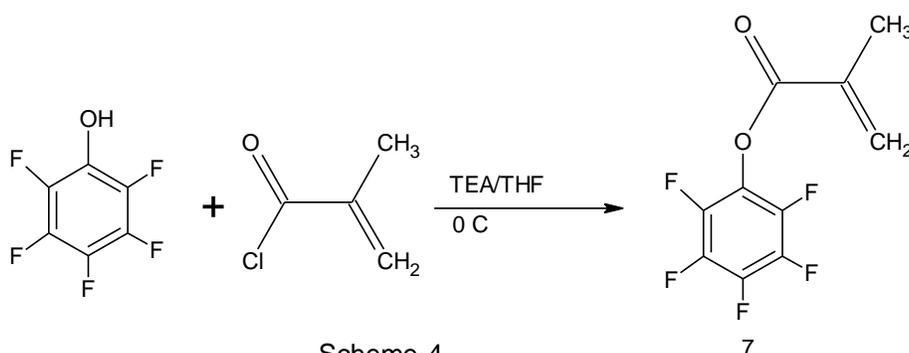
Scheme-2

We have also synthesized another important phosphonic acid derivative of substituted phenyl group starting from ethyl bromobenzene and dibutyl phosphate as reactants. One may note the difference in the substitution in the starting material. The overall yield for this reaction is around 70%.



Scheme-3

The fluorine substituted benzene derivatives received the renovated interest for the application in the field of polymers and in the energy harvesting technologies. Therefore we have synthesized the perfluoro phenyl methacrylate from perfluorophenyl. This can act as a monomer for the fluoro phenyl polymers. The reaction proceeds under normal conditions with considerably high yield as shown in the Scheme-4.



Scheme-4

APPLICATIONS

The synthesized compounds may have a application in nanometer scale control of material composition and properties in the solar energy harvesting system. If coated on ITO, it may act as the efficient electron transporter, thereby increasing the efficiency of energy conversion.

CONCLUSIONS

We have reported a straightforward and versatile route for the high yield synthesis of many phosphonic acid linkers to control both the ligating functionality, as well as providing the steric electronic effect through benzene ring between ligating and polymerizable groups. For the first time we have also reported the perfluoro phenyl methacrylate, a monomer for the potential polymeric application. These derivatives have a potential application as tethers to the SC-NP surfaces that promote the efficient electron transfer. Further investigations on the applicability of these compounds along with developing other possible compounds of same application are underway.

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AUTHOR ADDRESS

1. **Dr. M.K. Amshumali**

Assistant Professor, Department of Chemistry/Industrial Chemistry.

Vijayanagara Sri Krishnadevaraya University

Jnanasagara campus. Cantonment, Ballari-583105

Email: amshumali@vskub.ac.in, Phone: (0) 9481968706