Methodology Report: Sodium Dodecylphosphonate: An Efficient Anionic Surfactant for the Green Synthesis of α-Hydroxy Phosphonates in Micellar Media

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ABSTRACT

A simple and green synthesis of α-hydroxy phosphonates has been performed by reaction between aldehydes and triethyl phosphite using sodium dodecylphosphonate as anionic surfactant in micellar media under reflux conditions. The novel structures were recognized by 1H NMR, 13C NMR and 31P-NMR. The employ of green media, clean reaction profiles, simple experimental and work up procedures and high yields are some of the unique features of this process.

1. Introduction

Water is the cheapest, most plentiful and non-toxic chemical in environment. So, the use of water as reaction media is very important in organic synthesis. On the other hand, surfactants are one of the most important materials that find applications in almost every chemical industry including: detergents, paints, dyestuffs, cosmetics, pharmaceuticals, agrochemicals, fibers and plastics [1]. These compounds have bi-functional chemical structure. Therefore, these can cause that the organic reactions be performed in aqueous media in the Critical Micelle Concentration point (CMC). Sodium dodecylphosphonate (Na_2DP) is a solid alkaline surfactant. Here in, we have used this micelle as efficient micellar and basic catalyst for synthesis of α-hydroxy phosphonates. These families of organic compounds are fascinating of organic chemists due to a wide range of biological and pharmacological actions such as antibacterial [2], and antioxidant [3] (Figure 1).

Also, these compounds are important pesticides [4] and use as precursors for synthesis of the other types of α-functionalized phosphonates [5]. Many synthetic methods exist for the synthesis of α-hydroxyphosphonates including the nucleophilic addition of di- or trialkylphosphite to different carbonyl compounds in the presence of a variety of catalysts, such as, enzymatics [6], alkaloids [7], phosphoric acids [8], Lewis acids [9], alumina [10], Salalen [11], Salen [12], Binol [13], alumina/potassium fluoride [14], NH_4VO_3 [15], polymer/solid supported base [16], tethered bis(8-quinolinolato) (TBOx) aluminum (III) complexe [17], $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$

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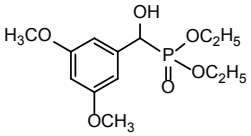
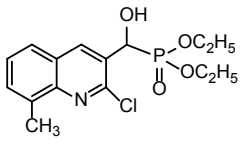


Antioxidant agent



Antibacterial agent

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Figure 1. Structures of α-hydroxy phosphonates

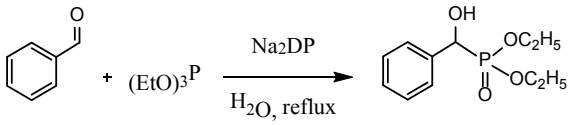

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Figure 2. Model reaction for this synthesis

Table 1. Effect of various amounts of Na_2DP in the preparation of α-hydroxy phosphonates.

Entry	Na_2DP (mmol)	Time (h)	Conversion (%)
1	0.05	24	0.0
2	0.12	24	0.0
3	0.35 (CMC point)	2	100
4	0.5	1	100
5	0.8	1	100
6	1	1	100

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[18], pyridine 2,6-dicarboxylic acid [19], Amberlyst-15 [20], hydrogen chloride [21], Chitosan [22], sodium-modified fluorapatite [23], oxone [24], 1,4-dimethylpiperazine [25], and rare-earth metal amido complexes [26]. Synthesis of these compounds is especially important that there is still a need to search for better catalysts. Lastly, these compounds were prepared by using of ultrasound in solvent-free and catalyst-free conditions [27]. As part of our present studies on the appliations of dodecylphosphonic acid salts, we have shown that sodium dodecylphosphonat is effective micellar catalyst for the synthesis of α-hydroxy phosphonates.

2. Discussion

The present paper describes a green and simple method for the synthesis of α-hydroxyphosphonates catalyzed by sodium dodecylphosphonate. Formerly, the critical micelle concentration of sodium dodecylphosphonate was determined in pure water by conductometry method. The CMC was obtained 1.6 mM [28]. At first, the ability of sodium dodecylphosphonate in the reaction between benzaldehyde (1 mmol) and triethyl phosphite (1.1 mmol) in water under reflux conditions was investigated (Figure 2). The best result was obtained in 1.4 CMC (3.2 mg, 0.5 mmol) of Na_2DP (Table 1, entry 4). Increasing the amount of catalyst did not show any improvement in the yield or reaction time. The optimized conditions were used to produce other α-hydroxyphosphonates (Figure 3 and Table 2).

As seen in Table 2, aromatic aldehydes bearing electron-withdrawing groups are reacted in high yields. We have also examined reaction between aromatic aldehydes bearing electron-donating groups such as p-Anisaldehyde and p-Methylbenzaldehyde with triethylphosphite in the same conditions. Our observation shows that these compounds do not react and the starting material was isolated intact after 24 h. Then, we investigated the reaction between benzaldehyde, derivatives of benzoxazole, benzimidazole and benzothiazole (1 mmol) and triethyl phosphite (1.1 mmol) (Table 2, entries 10, 11 and 12). The reaction was completed in 24 h and the desired products were characterized by ^{1}H NMR, ^{13}C NMR and ^{31}P-NMR.

3. Conclusion

In this paper, a selective, efficient, green and safe methodology for the preparation of α-hydroxy phosphonates was reported. Also, this method offer several additional advantages such as high conversion, employ of green media, clean reaction profiles, simple experimental and work up procedures.

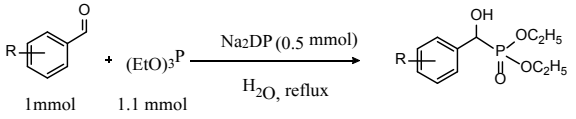

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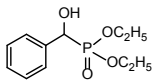
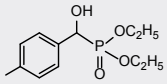
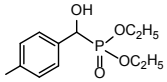
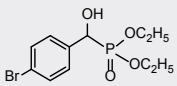
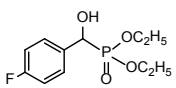
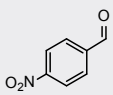
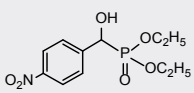
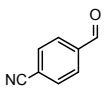
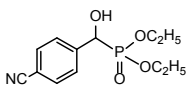
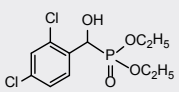
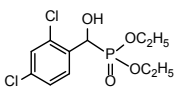
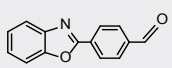
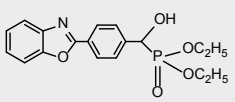
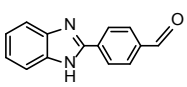
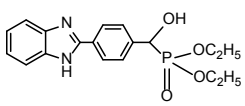
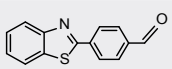
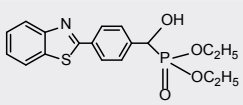
Figure 3. Optimized condition for this synthesis

Table 2. Synthesis of α-hydroxy phosphonates in the presence of Na_2DP in water

Entry	Aldehyde	Product	Isolated Yield (%)	Time (min)	M.P. (°C)	
					Found.	Lit
1			95	45	77	75-76[23]
2			90	90	127	25-127[23]
3			95	20	66	67-68[23]
4			93	60	Semi solid[23]	
5			85	20	Semi solid[23]	
6			90	24	87	87-88[23]
7			95	60	Semi-solid –	
8			85	45	Semi-solid –	
9			86	24	70	70-71[24]
10			77	24	Semi-solid –	
11			80	24	Semi-solid –	
12			68	24	Semi-solid –	

Experimental section

NMR spectra were recorded on Ultra Sheild Bruker 400 and Bruker Avance DPX-250 MHz. Melting points were determined in open capillary tubes in a Büchi-545 circulating oil melting point apparatus. Material purchased from Fluka, Aldrich and Merck Chemical Companies.

General preparation of α-hydroxy phosphonates

A mixture of aldehyde (1 mmol), triethylphosphite (1.1 mmol) and sodium dodecylphosphonate (0.5 mmol) was added to 5 ml of water. The reaction mixture was heated at 100 °C for the appropriate time (Table 2). With progress of the reaction, the corresponding product was pre-

cipitated in reaction vessel. Completion of the reaction was determined by TLC. Then the mixture was centrifuged and filtrated. The solid product was isolated without any more purification.

Supplementary Material

Diethyl ((4-bromophenyl) (hydroxy) methyl) phosphonate (Table 2, entry 4). Semi solid, ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm): 1.00-1.41 (m, 6H, 2-OCH_2CH_3), 3.75 (s, 1H, OH), 3.94-4.16 (m, 4H, 2-OCH_2CH_3), 4.98-5.02 (d, *J*=10.6 Hz, 1H, -CH-PO-), 7.26-7.52 (m, 4H, arom).

Diethyl (4-fluorophenyl) (hydroxy) methylphosphonate (Table 2, entry 5). Semi solid, ^{1}H-NMR (400 MHz, $CDCl_3$, δ/ppm): 1.20-1.27 (m, 6H, 2-OCH_2CH_3), 3.96-4.07 (m,4H,2-OCH_2CH_3), 4.51 (s, 1H, OH), 4.98-5.00 (d, *J*=10.0 Hz 1H, -CH-PO-), 7.02-7.06 (m, 2H, arom), 7.26-7.47(m, 2H, arom).

Diethyl ((4-cyanophenyl) (hydroxy) methyl) phosphonate (Table 2, entry 7). Semi solid, ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm): 11.01-1.19 (m, 6H, 2-OCH_2CH_3), 2.12 (s, 1H, OH), 3.89-4.04 (m, 4H, 2-OCH_2CH_3), 5.82-5.92 (d, *J*=9.2 HZ, 1H, -CH-PO-), 7.15-7.18 (m, 1H, arom), 7.37-7.40 (m, 2H, arom), 7.56-7.60 (m, 1H, arom).

Diethyl ((2,3-dichlorophenyl) (hydroxy) methyl) phosphonate (Table 2, entry 8). Semi solid, ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm): 1.12-1.34 (m, 6H,2 -OCH_2CH_3), 3.94-4.08 (m, 4H, 2-OCH_2CH_3), 6.20-6.25 (d, *J*=13.0 Hz, 1H, -CH-PO-), 7.19-7.96 (m, 2H, arom), 7.97-8.00 (m, 1H, arom).

Diethyl ((4-(benzoxazol-2-yl)phenyl) (hydroxy) methyl) phosphonate (Table 2, entry 10). Semi- solid, ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm): 1.00-1.39 (m, 6H, 2-OCH_2CH_3), 2.4 (s, 1H, OH), 3.94-4.11 (m, 4H, 2-OCH_2CH_3), 4.98-5.02 (d, *J*=10.6 Hz, 1H, -CH-PO-), 7.16-7.34 (m, 4H, arom), 7.37-7.41 (m, 2H, arom), 7.57-7.75 (m, 2H, arom). ^{13}C-NMR (100 MHz, $CDCl_3$, δ/ppm): 17.58 (-OCH_2CH_3), 54.45 (-OCH_2CH_3), 70.69-72.28 (d, $^{1}J_{CP}$=158.8 Hz, -CH-PO-), 110.7, 122.0, 126.7, 128.4, 131.6, 132.8, 133.8, 135.4, 149.4, 151.0, 159.6, 161.2. ^{31}P NMR (162 MHz, $CDCl_3$, δ /ppm):-19.97.

Diethyl ((4-(1H-benzimidazol-2-yl)phenyl) (hydroxy)methyl) phosphonate (Table 2, entry 11). Semi-solid, ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm): 1.16-1.18 (m, 6H, -OCH_2CH_3), 4.02-4.06 (m, 4H, -OCH_2CH_3), 5.46 (s, 1H, OH), 5.56-5.61 (d, *J*=11.7 Hz, 1H, -CH-PO-), 7.31-7.34 (m, 2H, arom), 7.58-7.95 (m, 4H, arom), 8.11-8.14 (m, 2H, arom), 9.99 (s, brs., 1H, NH). ^{13}C-NMR (63 MHz, $CDCl_3$, δ/ppm): 16.45-16.53 (-OCH_2CH_3), 62.52-62.63 (-OCH_2CH_3), 71.42-73.72 (d, $^{1}J_{CP}$=144.9 Hz, -CH-PO-), 110.55, 115.45, 117.07, 119.33, 127.00, 131.42, 137.22, 149.23, 160.50. ^{31}P NMR (162 MHz, $CDCl_3$, δ /ppm):-19.96.

Diethyl ((4-benzothiazol-2-yl)phenyl) (hydroxy) methyl) phosphonate (Table 2, entry 12). Semi- solid, ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm): 1.18-1.40 (m, 6H, 2-OCH_2CH_3), 4.03-4.30 (m, 4H, 2-OCH_2CH_3), 4.95-5.06 (d, *J*=29.2 Hz, 1H, -CH-PO-), 5.30 (s, 1H, OH), 7.38-7.47 (m, 4H, arom), 7.70-8.15 (m, 4H, arom). ^{13}C-NMR (100 MHz, $CDCl_3$, δ/ppm): 18.50 (-OCH_2CH_3), 54.33 (-OCH_2CH_3), 77.76-79.06 (d, $^{1}J_{CP}$=130.2 Hz, -CH-PO-), 110.58, 115.97, 125.01, 125.05, 128.6, 144.3, 148.2, 161.0, 166.6, 167.2. ^{31}P NMR (162 MHz, $CDCl_3$, δ /ppm):-19.90.

Acknowledgements

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Conflict of Interest

The authors declared no conflict of interests.

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