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ORIGINAL ARTICLE

# An efficient method for synthesis of stable phosphorus ylides and 1,4-diionic organophosphorus compounds in the presence of sodium dodecyl sulfate in aqueous media

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**KEYWORDS**

Stable phosphorous ylides;
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Sodium dodecyl sulfate;
Aqueous media

**Abstract** Stable crystalline phosphorus ylides and 1,4-diionic organophosphorus compounds were obtained in good to excellent yields from the 1:1:1 addition reaction between triphenylphosphine, dialkyl acetylenedicarboxylates and β-dicarbonyl or heterocyclic compounds, such as diethyl malonate, acetyl acetone, 1,3-diphenyl propane-1,3-dione, 1,3-dimethylbarbituric acid, meldrum's acid, 2-benzoxazolinone, benzotirazole, and 2-thiazoline-2-thiol in the presence of sodium dodecyl sulfate as a surfactant in water. Green synthesis, mild conditions, decreasing timescale of reaction, low cost, and easy workup are the main advantages of this method.



## 1. Introduction

With the increasing environmental concerns and the regulatory constraints faced by the chemical and pharmaceutical industries, development of environmentally benign organic reactions has become a crucial and demanding research area in modern organic chemical research (Anastas, 1998). Therefore, more and more chemists are devoted to the researching "green synthesis" which means the reagent, solvent, and surfactant are environmentally friendly in the organic chemical reactions. Recently, organic reactions in water without use of harmful organic solvents have attracted much attention, because water is a cheap, safe, and environmentally benign solvent (Yavari and Islami, 1998; Yavari et al., 1999). Previously, the scant solubility of reactants was the main reason preventing the use of water as a green solvent. Various reactions that are traditionally carried out in organic solvents have been equally successful or even more effective in aqueous media (Venkatraman and Li, 2001; Tian et al., 2001). The use of water as a green solvent in organic reaction in place of commonly used organic solvents has been reported in the filed of green chemistry (Breslow and Maitra, 1984; Delair and Luche, 1989). This advantage prompted us to use towards the synthesis of stable phosphorus

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ylides and 1,4-diionic organophosphorus compounds in the presence of sodium dodecyl sulfate in aqueous media.

## 2. Experimental

Dialkyl acetylenedicarboxylates, diethyl malonate, acetyl acetone, 1,3-diphenyl propane-1,3-dione, 1,3-dimethylbarbituric acid, meldrum's acid, 2-benzoxazolinone, benzotirazole, 2-thiazoline-2-thiol, triphenylphosphine, and sodium dodecyl sulfate were obtained from Fluka or Merck companies, and used without additional purification. Melting points were measured by Electrothermal 9100 apparatus. IR spectra were recorded on a Shimadzu IR-460 spectrometer (pellets with KBr). $^1$H NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer instrument with $CDCl_3$ as solvent.

### *2.1. General procedure for preparation of stable phosphorous ylides and 1,4-diionic organophosphorus compounds*

To a magnetically stirred solution of a C–H or N–H acid (1 mmol) in water (5 mL), a mixture of triphenylphosphine (0.26 g, 1 mmol) and sodium dodecyl sulfate (0.009 g, 0.1 mmol) was added. Then dimethyl acetylenedicarboxylate (0.14 g, 1 mmol) was added, dropwise, at room temperature for more than 10 min. After approximately 1–2 h stirring, the solution was filtered and the solid phase washed with dichloromethane. The solvent evaporated under reduce pressure and colorless precipitate washed with cold diethyl ether.

### *2.2. Selected specteral data*

#### *2.2.1. Dimethyl 2-[di(ethoxycarbonyl) methyl]-3-(triphenylphosphoranylidene)-butane-1,4-dioate (**3a**)*

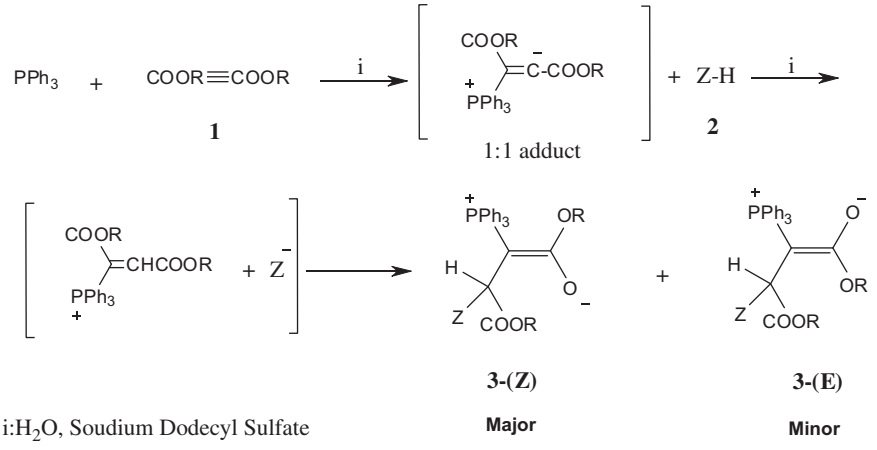
Colorless crystals, m.p. 192–193 °C, yield: (80%), IR (KBr) ($t_{max}$, cm$^{-1}$): 1760, 1750, 1741, 1635 (C═O). *Major isomer*(*Z*)-**3a** (60%), $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ 1.19 (6H, t, $^3J_{HH}$ = 6.8 Hz, $2CH_3$), 3.06 and 3.60 (6H, 2s, $2OCH_3$), 3.38 (1H, dd, $^3J_{HH}$ = 10.4 Hz, $3J_{PH}$ = 17.7 Hz, P═C–CH), 4.00 and 4.13 (4H, 2m, $2OCH_2$), 4.63 (1H, d, $^3J_{HH}$ = 10.4 Hz, $CH(CO_2Et)_2$), 7.40–7.70 ($15H_{arom}$, m, $3C_6H_5$). *Minor isomer* (*E*)-**3a** (40%), $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ 1.20 (6H, t, $^3J_{HH}$ = 6.8 Hz, $2CH_3$), 3.50 and 3.71 (6H, 2m, $2OCH_3$), 3.33 (1H, dd, $^3J_{HH}$ = 10.4 Hz, $^3J_{PH}$ = 18.0 Hz, P═C–CH), 3.85 and 3.87 (4H, 2s, $2OCH_2$), 4.87 (1H, d, $^3J_{HH}$ = 10.8 Hz, $CH(CO_2Et)_2$, 7.40–7.70 ($15H_{arom}$, m, $3C_6H_5$).

#### *2.2.2. Diethyl 2-(2-mercopto-2-thiazoline-3-yl)-3-(triphenylphosphoranylidene)-butanedioate (**3p**)*

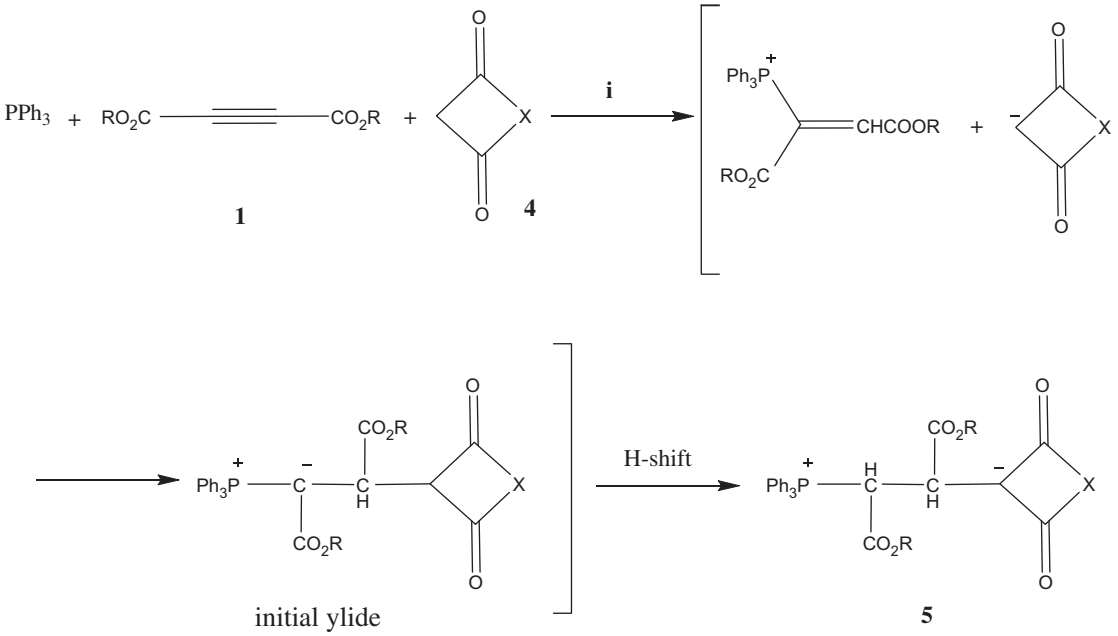
White powder, m.p. 111–112 °C, yield: (80%), IR(KBr) ($t_{max}$, cm$^{-1}$): 1750 and 1638 (C═O), 1460 (C═S). *Major isomer*(*Z*)-**3p** (75%), $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ 0.43 and 1.30 (6H, 2t, $^3J_{HH}$ = 7.0 and 7.2 Hz, $2CH_3$), 3.20 (2H, m, $CH_2N$), 3.49–4.35 (4H, m, $2OCH_2$), 4.44 (2H, m, $CH_2S$), 5.39 (1H, d, $^3J_{PH}$ = 17.8 Hz, P═C–CH), 7.48–7.69 ($15H_{arom}$, m, $3C_6H_5$). *Minor isomer* (*E*)-**3p** (25%), $^1$H NMR (500.1 MHz, $CDCl_3$): δ 1.17 and 1.20 (6H, 2t, $^3J_{HH}$ = 7.0 and 7.2 Hz, $2CH_3$), 3.30 (2H, m, $CH_2N$), 3.49–4.35 (4H, m, $2OCH_2$), 4.60 (2H, m, $CH_2S$), 5.37 (1H, d, $^3J_{PH}$ = 19.2 Hz, P═C–CH), 7.48–7.69 ($15H_{arom}$, m, $3C_6H_5$).

#### *2.2.3. Diethyl 2-(1,3-dimethylbarbituric acid-5-yl)-3-(triphenylphosphoranylidene)-butane-1,4-dioate (**5b**)*

Colorless crystals, m.p. 154–156 °C, yield: (70%), IR (KBr) ($t_{max}$, cm$^{-1}$): 1713, 1659, 1582 (C═O). *Major isomer*- **5b** (70%), $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ 0.72 (3H, t, $^3J_{HH}$ = 7.3 Hz, $CH_3$), 0.82 (3H, t, $^3J_{HH}$ = 6.9 Hz, $CH_3$), 2.92 (6H, s, $2NCH_3$), 3.63 and 3.72 (4H, m, $2OCH_2$), 4.97 (1H, dd, $^3J_{HH}$ = 10.3 Hz, $^3J_{PH}$ = 5.3 Hz, P–CH–CH), 5.79 (1H, dd, $^3J_{HH}$ = 10.3 Hz, $^2J_{PH}$ = 10.8 Hz, P–CH–CH), 7.55–8.05 ($15H_{arom}$, m, $3C_6H_5$). $^{13}$C NMR (125.77 MHz, $CDC1_3$): 13.69, 13.96 ($2CH_3$), 27.21 ($2NCH_3$), 43.40 (d, $^1J_{PC}$ = 40.0 Hz, P–CH), 44.49 (d, $^2J_{CP}$ = 4.7 Hz, P–CH–CH), 61.70, 62.44 ($2OCH_2$), 82.60 [d, $^3J_{CP}$ = 11.7 Hz, $C(CO)_2$], 121.65 (d, $^1J_{CP}$ = 88.0 Hz, $C_{ipso}$), 129.70 (d, $^3J_{CP}$ = 12.8 Hz, $C_{meta}$), 134.00 ($C_{para}$), 134.40 (d, $^2J_{CP}$ = 9.0 Hz, $C_{ortho}$), 153.83 (C═O, urea), 162.78 (O═C–C–C═O), 167.07, 173.99 (2C═O, ester). *Minor isomer*- **5b** (30%), $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ 0.83 (3H, t, $^3J_{HH}$ = 6.7 Hz, CH3), 1.10 (3H, t, $^3J_{HH}$ = 7.0 Hz, $CH_3$), 3.27 (6H, s, $2NCH_3$), 3.45 and 4.03 (4H, m, $2OCH_2$), 5.03 (1H, dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{PH}$ = 6.3 Hz, P–CH–CH), 5.89 (1H, dd, $^3J_{HH}$ = 11.4 Hz, $2J_{PH}$ = 15.4 Hz,




**Scheme 1** Synthesis of stable phosphorus ylides **3a**–**q** involving two rotational isomers **3**-(*Z*) and **3**-(*E*) in the presence of sodium dodecyl sulfate in water at room temperature.




i:$H_2O$, Soudium Dodecyl Sulfate

**Scheme 2** Synthesis of 1,4-diionic organophosphorus compound **5a**–**f** in the presence of sodium dodecyl sulfate in water at room temperature.

P–CH–CH), 7.55–8.05 ($15H_{arom}$, m, $3C_6H_5$). $^{13}C$ NMR (125.77 MHz, $CDC1_3$): 13.58, 14.40 ($2CH_3$), 27.55 ($2NCH_3$), 41.82 (P–CH–CH), 42.31 (d, $^1J_{PC}$ = 48.6 Hz, P–CH), 61.29, 62.35 ($2OCH_2$), 83.39 [d, $^3J_{CP}$ = 2.3 Hz, $C(CO)_2$], 118.47 (d, $^1J_{CP}$ = 86.6 Hz, $C_{ipso}$), 129.49 (d, $^3J_{CP}$ = 13.0 Hz, $C_{meta}$), 134.40 (d, $^2J_{CP}$ = 7.7 Hz, $C_{ortho}$), 134.48 ($C_{para}$), 152.90 (C═O, urea), 163.08 (O═C–C–C═O), 167.10, 173.25 (2C═O, ester).

**Table 1** Synthesis of stable phosphorus ylides **3a**–**q** in the presence of sodium dodecyl sulfate in water at room temperature.

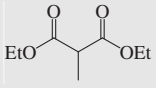
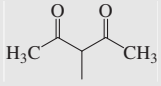
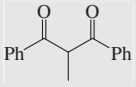
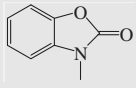
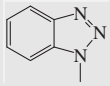
| Entry | *Z* | R | 3 | Yield% | M.p. (°C) | References |
|---|---|---|---|---|---|---|
| 1 |  | Me | **3a** | 80 | 192–193 | Islami et al. (2002) |
| 2 | | Et | **3b** | 70 | 165–166 | Islami et al. (2002) |
| 3 |  | Me | **3c** | 80 | 173–175 | Islami et al. (2002) |
| 4 | | Et | **3d** | 70 | 165–167 | Islami et al. (2002) |
| 5 | | t-Bu | **3e** | 80 | 145–148 | Yavari et al. (2003) |
| 6 |  | Me | **3f** | 80 | 205–206 | Yavari and Islami (1997) |
| 7 | | Et | **3g** | 78 | 208–209 | Yavari and Islami (1997) |
| 8 | | t-Bu | **3h** | 80 | 207–209 | Yavari and Islami (1997) |
| 9 |  | Me | **3i** | 85 | 162–164 | Maghsoodlou et al. (2006b) |
| 10 | | Et | **3j** | 80 | 184–186 | Maghsoodlou et al. (2006b) |
| 11 | | t-Bu | **3k** | 82 | 192–194 | Maghsoodlou et al. (2006b) |
| 12 |  | Me | **3l** | 88 | 144–146 | Maghsoodlou et al. (2006c) |
| 13 | | Et | **3m** | 72 | 148–150 | Maghsoodlou et al. (2006c) |
| 14 | | t-Bu | **3n** | 82 | 155–157 | Maghsoodlou et al. (2006c) |
| 15 |  | Me | **3o** | 80 | 155–157 | Maghsoodlou et al. (2005) |
| 16 | | Et | **3p** | 75 | 111–112 | Maghsoodlou et al. (2005) |
| 17 | | t-Bu | **3q** | 80 | 107–108 | Maghsoodlou et al. (2005) |

**Table 2** Synthesis of 1,4-diionic organophosphorus compound **5a–f** in the presence of sodium dodecyl sulfate in water at room temperature.

| Entry | X | R | 5 | Yield% | M.p. (°C) | References |
|---|---|---|---|---|---|---|
| 1 | $-CH_3N-CO-NCH_3-$ | Me | **5a** | 77 | 161–163 | Yavari et al. (1999) |
| 2 | $-CH_3N-CO-NCH_3-$ | Et | **5b** | 70 | 155–156 | Yavari et al. (1999) |
| 3 | $-CH_3N-CO-NCH_3-$ | t-Bu | **5c** | 82 | 154–156 | Maghsoodlou et al. (2006a) |
| 4 | $-O-C(CH_3)_2-O-$ | Me | **5d** | 78 | 182–183 | Yavari et al. (1999) |
| 5 | $-O-C(CH_3)_2-O-$ | Et | **5e** | 70 | 163–166 | Yavari et al. (1999) |
| 6 | $-O-C(CH_3)_2-O-$ | t-Bu | **5f** | 80 | 181–183 | Yavari et al. (1999) |

*2.2.4. Dimethyl 2-(2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-yl)-3-(triphenylphosphoranylidene)-butane-1,4-dioate(**5d**)*
Colorless crystals, m.p. 182–183 °C, yield: (78%), IR (KBr) ($t_{max}$, $cm^{-1}$): 1745, 1735 (C=O). *Major isomer*-**5d** (80%), $^1H$ NMR (500.1 MHz, $CDCl_3$): $\delta$ 1.65 (6H, s, $2CH_3$), 3.27 and 3.31 (6H, 2s, $2OCH_3$), 4.79 (1H, dd, $^3J_{HH}$ = 10.7 Hz, $^3J_{PH}$ = 4.4 Hz, P–CH–CH), 5.70 (1H, dd, $^3J_{HH}$ = 10.9 Hz, $^2J_{PH}$ = 11.0 Hz, P–CH–CH), 7.56–8.10 ($15H_{arom}$, m, $3C_6H_5$). *Minor isomer*-**5d** (20%), $^1H$ NMR (500.1 MHz, $CDCl_3$): $\delta$ 1.29 (6H, s, $2CH_3$), 3.29 and 3.55 (6H, 2s, $2OCH_3$), 4.90 (1H, dd, $^3J_{HH}$ = 11.8 Hz, $^3J_{PH}$ = 3.7 Hz, P–CH–CH), 5.84 (1H, dd, $^3J_{HH}$ = 12.0 Hz, $^2J_{PH}$ = 13.8 Hz, P–CH–CH), 7.56–8.10 ($15H_{arom}$, m, $3C_6H_5$).

## 3. Results and discussion

The reaction between triphenylphosphine, acetylenic esters **1** and β-dicarbonyl or heterocyclic compounds (**2, 4**) leds to the corresponding stable phosphorus ylides **3a–q** or 1,4-diionic organophosphorus compounds **5a–f** in the presence of sodium dodecyl sulfate as a surfactant in water in good to excellent yields (Schemes 1 and 2).

Based on the well established chemistry of trivalent phosphorus nucleophiles, it is reasonable to assume that phosphorus ylide **3** is formed due to the initial addition of triphenylphosphine to the acetylenic ester **1** and concomitant protonation of 1:1 adduct by the β-dicarbonyl compounds or heterocyclic compounds, such as diethyl malonate, acetyl acetone, 1,3-diphenyl propane-1,3-dione, 2-benzoxazolinone, benzotirazole, and 2-thiazoline-2-thiol) (Scheme 1), whereas 1,4-diionic organophosphorus compound **5** is formed because of the proton shift in initial ylide when β-dicarbonyl compounds such as 1,3-dimethylbarbituric acid, meldrum's acid, are used as the heterocyclic compounds (Scheme 2). The results are summarized in Tables 1 and 2.

A comparison of the results obtained from aqueous media with organic solvent media, same phosphorus ylides and 1,4-diionic organophosphorus compounds were synthesized in organic solvents. The results were identical with those that obtained in aqueous media. The spectral data and physical properties of the phosphoranes **3a–q** and 1,4-diionic organophosphorus compounds **5a–f** were in a good agreement with those that reported in literature (Maghsoodlou et al., 2006a,b,c, 2005; Islami et al., 2002; Yavari et al., 1999, 2003; Yavari and Islami, 1997).

## 4. Conclusion

For the first time sodium dodecyl sulfate has been employed for a convenient and rapid synthesis of phosphorous ylides and 1,4-diionic organophosphorus compounds in aqueous media. Although, the yields of stable phosphorous ylides or 1,4-diionic organophosphorus compounds are low in comparison with the corresponding products that obtained in the presence of organic solvents, but the reaction times are considerably shorter and also the use of water as a green solvent has some advantages including low cost, non-falmability and its non-toxic.

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