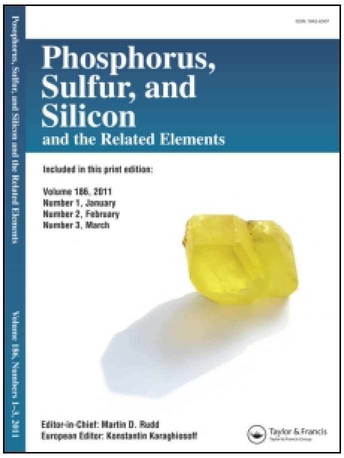

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Synthetic Utilization of α-Phosphonovinyl Anions

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The α-phosphonovinyl anions, generated in situ from treatment of β-hetero-substituted vinylphosphonates **1a-c** with LDA (or LTMP), were trapped with various electrophiles such as chlorotriorganosilanes, chlorotrimethylgermane, chlorotriorganotins, dimethyl disulfide, and halogen to afford the corresponding β-hetero-substituted α-functionalized vinylphosphonates **2–14** in good to excellent yields. The Friedel-Crafts reaction of α-(silyl) or α-(germyl)phosphonoketene dithioacetals **2**, **9** or **4** with acid chlorides gave α-acylated phosphonoketene dithioacetals **15–19** in 53–91 % yields. The palladium-catalyzed cross-coupling reaction of β-ethoxy-α-(tributylstannyl)vinylphosphonate **13** with a variety of organic halides (R = acyl, allyl, aryl etc.) provided β-ethoxy-α-substituted vinylphosphonates **20–25** in good to moderate yields. The palladium-mediated cross-coupling reaction of α-(iodo)-vinylphosphonates **7**, **14** with terminal acetylenes afforded α-alkynylated vinylphosphonates **26–29** in 69–83 % yields.

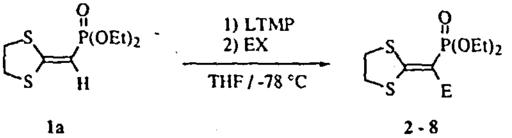
Keywords: α-phosphonovinyl anions; α-(triorganomatal)vinylphosphonates; α-(alkynyl)vinylphosphonates; Pd-catalyzed cross-coupling; Friedel-Crafts reacton

INTRODUCTION

Vinylphosphonates containing various functional groups have been widely studied due to their synthetic and biological usefulness.[1] We have recently reported the generation of α-carbanions of phosphonoketene dithioacetals and their synthetic application to dithioallenes.[2] We report here a new convenient synthesis of various vinylphosphonates containing synthetically useful substituents such as organometallic groups and halogen on the α-carbon *via* α-phosphono-stabilized vinyl anions, and also the synthesis of a new class of vinylphosphonates *via* functional group transformation of the resulting α-functionalized vinylphosphonates.

Results and Discussion

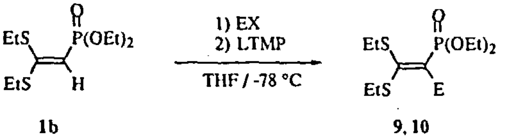
The 2,2-(ethylenedithio)-1-phosphonovinyl anion, generated from phosphonoketene dithioacetal **1a** and lithium 2,2,6,6-tetramethylpiperidide (LTMP) at -78 °C for 1h, was treated with a wide variety of electrophiles to provide α-functionalized phosphonoketene dithioacatals **2-8** in good yields (eq 1).



(1)

2 : E = $SiMe_3$ (81 %)
3 : = $SiPh_3$ (69 %)
4 : = $GeMe_3$ (78 %)
5 : = $SnPh_3$ (69 %)
6 : E = SMe (76 %)
7 : = I (83 %)
8 : = Br (55 %)

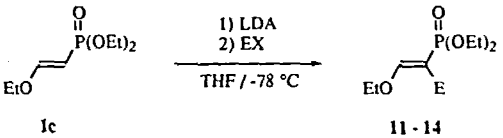
In the case of acyclic dithioacetal **1b**, a THF solution of LTMP was inversely added to the mixture of **1b** and an electrophile (Me_3SiCl or Bu_3SnCl) at -78 °C to give the expected α-triorganometal-substituted phosphonoketene dithioacetal **9** or **10** in good yields (eq 2).



(2)

9 : E = $SiMe_3$ (64 %)
10 : = $SnBu_3$ (83 %)

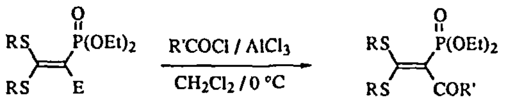
Treatment of **1c** with LDA in THF at -78 °C followed by addition of an electrophile similarly led to α-substituted β-(ethoxy)vinylphosphonates **11-14** in high yields (eq 3).



(3)

11 : E = $SiMe_3$ (96 %)
12 : = $Si\textit{t}\text{-}BuMe_2$ (75 %)
13 : E = $SnBu_3$ (80 %)
14 : = I (91 %)

We next tried to develop multipurpose vinylphosphonates *via* the above prepared α-functionalized vinylphosphonates. The Friedel-Crafts reaction of **2**, **4** and **9** with acid chlorides (2 equiv) / $AlCl_3$ (2 equiv) led to α-acylated phosphonoketene dithioacetals **15-19** in 53-91 % yields (eq 4).



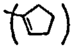
(4)

2, 4, 9

15 - 19

15 : R R =$(CH_2)_2$, R'= Me (89 %)

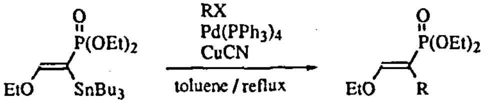
16 : R R =$(CH_2)_2$, R'= CH=CHMe (91 %)

17 : R R =$(CH_2)_2$, R'=  (91 %)

18 : R R =$(CH_2)_2$, R'= Ph (89 %)

19 : R = Et, R' = Ph (53 %)

Since the synthesis of α-acylated β-(ethoxy)vinylphosphonates are not accessible by the Friedel-Crafts reaction of **11** with acid chlorides as above, the Stille cross-coupling reaction of **13** with benzoyl chloride in the presence of $Pd(PPh_3)_4$ (4 mol%) and CuCN (9 mol%) was carried out to give the desired α-benzoylated β-(ethoxy)vinylphosphonate **20** (eq 5). Similar treatment of **13** with various organic halides produced cross-coupling products **21-25** (eq 5).



(5)

13

20 - 25

20 : R = COPh (87 %)

21 : R = COOEt (76 %)

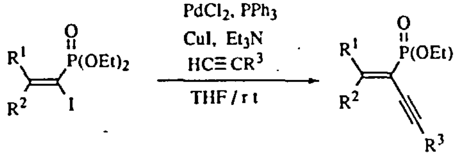
22 : R = $CH_2CH=CH_2$ (47 %)

23 : R = Ph (79 %)

24 : R = *o*-C_6H_4CHO (97 %)

25 : R = *o*-$C_6H_4COCH_3$ (62 %)

We have also attempted to synthesize a new class of enyne compounds containing phosphorus and hetero functional group. The palladium-mediated cross-coupling reaction of **7** and **14** with terminal acetylenes in THF at room temperature afforded the desired enyne compounds **26-29** in good yields (eq 6). The above results have indicated that the palladium-mediated cross-coupling reaction of α-(iodo)vinylphosphonates with terminal acetylenes has no limitation in functionalities on the vinylphosphonates and the acetylenes.

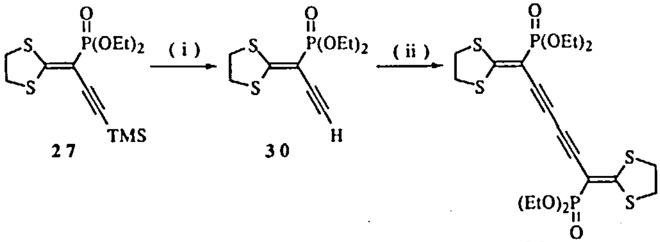


7, 14 **26 - 29**

(6)

26 : $R^1\ R^2 = S(CH_2)_2S$, $R^3 = Ph$ (73 %)
27 : $R^1\ R^2 = S(CH_2)_2S$, $R^3 = TMS$ (83 %)
28 : $R^1\ R^2 = S(CH_2)_2S$, $R^3 = CH_2OTHP$ (69 %)
29 : $R^1 = H$, $R^2 = OEt$, $R^3 = Ph$ (79 %)

Furthermore, oxdative homo-coupling of the terminal alkyne **30** derived from **27** produced the expected diene-diyne derivative **31** in excellent yield (93 %)(eq 7).



27 **30** **31**

(7)

(i) TBAF (0.2 equiv), THF, 50 °C, 10 min, 98%.
(ii) $Cu(OAc)_2$ (4.4 equiv), THF-pyridine-EtOH, 70 °C, 30 min, 93 %.

References

[1] T. Minami and J. Motoyoshiya *Synthesis* 333 (1992).

[2] T. Minami, T. Okauchi, H. Matsuki, M. Nakamura, J. Ichikawa, and M. Ishida *J. Org. Chem.* 61, 8132 (1996).