Regioselective C-Acylation of Vinylphosphorus Compounds through Electroreduction or Mg-Promoted Reduction

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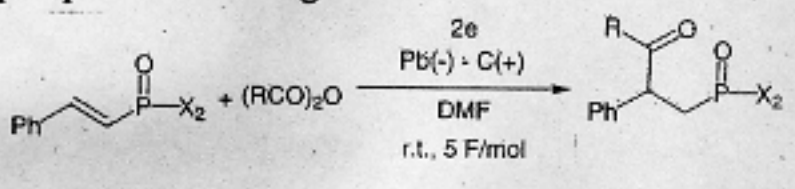
Phosphorus compounds are much usefulness as medicins, agrochemicals, plasticizers, fire retardants and heavy metal extraction agents because of their interesting properties and easy availability. Therefore, selective C-acylation using phosphonates or phosphine oxides as active electron-withdrawing groups of electron-deficient olefins may be an important and challenging subject in synthetic transformation.

In this study, we wish to report facile and regio-selective C-acylation of vinylphosphonate derivatives by either of electroreduction or Mg-promoted reduction in the presence of acylating agents to give the corresponding b-acylated products in good yields.

The electroreduction of starting substrates **1-4** was carried out using a divided cell equipped with a lead plate as the cathode and a carbon rod as the anode in the presence of large excess of acid anhydride **5a, b** in DMF containing tetraethylammonium *p*-toluenesulfonate as a supporting electrolyte until 5 F/ mol of electricity passed through the system. The corresponding β-acylated phosphonates **6-8** or phosphine oxide **9** were obtained in good yields, accompanying with a small amount of simply reduced products **10-13** as the by-products, as shown in Table 1.

Furthermore, Mg-promoted acylation of β-styrylphosphonates **1-3** and phosphine oxide **4** with acylating agents was found to give the similar results to those from the electrochemical method (Scheme 2). Thus, the reaction of **1-4** with acid anhydrides **5a-c** (15 eq.) in the presence of TMSCl (or acid chlorides **14** in the absent of TMSCl) in DMF took place using Mg turnings (6.0 eq.) for Grignard reaction without any pretreatment to give smoothly the corresponding β-acylated product **6-9** respectively in moderate to good yields accompanying with no simply reduced products **10-13** (Table 2). It is interesting that the present Mg-promoted C-acylation of diphenyl phosphonate **4** gave a satisfactory result (entry 8 and 14), showing a sharp contrast with the results from electroreduction.

As a conclusion, facile and regioselective acylation on the β-carbon atom of aromatic vinylphosphonate derivatives **1-4** was successfully accomplished by either of electroreduction or Mg-promoted electron-transfer reaction to give the β-ketophosphonates in good yields, which would formed by conjugated nuclophilic attack of difficulty available acyl anions or their chemical equivalents to **1**. The presence of a phosphonate group on a styrene moiety activates a olefinic bond for electron-transfer type of reductions, and also provides new type of phosphorus containing functional materials.



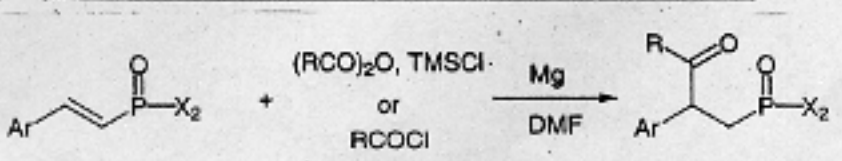
1 : X = OEt
2 : X = O*i*Pr
3 : X = OPh
4 : X = Ph

5a : R = Me
5b : R = Et

6 : X = OEt
7 : X = O*i*Pr
8 : X = OPh
9 : X = Ph

Table 1 Electroreduction of Compounds **1-4**

Entry	Substrate	R	Conv. (%)	Yield (%)
1	**1**	**5a**: Me	94	**6a**: 56 **10**: 13
2	**1**	**5b**: Et	100	**6b**: 41 **10**: -
3	**2**	**5b**: Me	85	**7a**: 46 **11**: 9
4	**2**	**5b**: Et	100	**7b**: 72 **11**: 7
5	**3**	**5b**: Et	75	**8b**: 5 **12**: 4
6	**4**	**5b**: Et	90	**9b**: 60 **13**: 18



1 : Ar = Ph, X = OEt
2 : Ar = Ph, X = O*i*Pr
3 : Ar = Ph, X = OPh
4 : Ar = Ph, X = Ph
14 : Ar = *m*-chlorophenyl, X = OPh

$(RCO)_2O$
5a : R = Me
5b : R = Et
5c : R = *n*-Pr

RCOCl **15b** : R = Et
15c : R = *n*-Pr

6 : Ar = Ph, X = OEt
7 : Ar = Ph, X = O*i*Pr
8 : Ar = Ph, X = OPh
9 : Ar = Ph, X = Ph
16 : Ar = *m*-chlorophenyl, X = OPh

Table 2 C-Acylation of Vinylphosphorus Compounds **1-4, 14**

Entry	Substrate	Acylating Agent	TMSCl	Yield (%)
1	1	**5a** $(MeCO)_2O$	1equiv	**6a**: 45
2	1	**5a** $(MeCO)_2O$	-	**6a**: 45[a]
3	1	**5b** $(EtCO)_2O$	1equiv	**6b**: 65
4	1	**5c** (*n*-$PrCO)_2O$	1equiv	**6c**: 62
5	2	**5a** $(MeCO)_2O$	1equiv	**7a**: 64
6	2	**5b** $(EtCO)_2O$	1equiv	**7b**: 50
7	2	**5c** (*n*-$PrCO)_2O$	1equiv	**7c**: 77
8	3	**5b** $(EtCO)_2O$	1equiv	**8b**: 51
9	4	**5b** $(EtCO)_2O$	1equiv	**9b**: 46
10	1	15b EtCOCl	-	**6b**: 56
11	2	15b EtCOCl	-	**7b**: 61
12	2	15c *n*-PrCOCl	-	**7c**: 61
13	3	15b EtCOCl	-	**8b**: 74
14	4	15b EtCOCl	-	**9b**: 53
15	14	15b EtCOCl	-	**16b**: 68

References

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