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LETTERS

Zinc Promoted Facile Method for the Acylation of Ylides at α-Carbon

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Abstract : Stabilised triphenylphosphonium ylides are acylated at the α-carbon with different acyl groups using zinc.

Ylides are a useful tool by which organic chemists extend a carbon chain by incorporating the double bond in the molecule.[1] Ylides can also be converted to many other functionalities such as ketones, carboxylic esters and aldehydes. In particular, triphenylphosphonium ylides are more popular because of their easy preparation and stability. This method of alkene synthesis leads to mixtures of E & Z alkenes. It is observed in the literature that substitution at the α-carbon in ylides can increase the E/Z ratio. Particularly, acyl substituted ylides have got more importance because of their utility in the synthesis of unsaturated ketones and cyclopropane pyrethroids.

There are few reported methods for the acylation of ylides at the α-carbon. One of the methods is performed by a transylidation[2,3] reaction where the one molecule of ylide used is lost as the triphenyl alkylphosphonium chloride. This stoichiometric reaction is carried out using triethylamine[4] or lithium salts[5] as bases. There are recent reports where phase transfer catalysts, NaOH[6a] and triflic anhydride, triethylamine[6b] are employed. In all these methods, the base used may cause problems to other protected functional groups, or yields are very low. So it is desirable to develop a method for acylation to avoid the use of base.

Recently, metal catalysed reactions[7] have gained wide popularity in organic synthesis because of their simple workup, activating or catalysing nature and selectivity. Among the transition metals, zinc[8] catalysis has gained wide popularity owing to the unique property of surface coordination with polar groups.[9] Recently we have demonstrated the zinc mediated esterification of acid chlorides,[10] and carbamate[11] formation and Friedel Crafts acylation.[12] In continuation of

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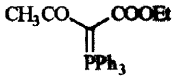
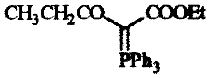
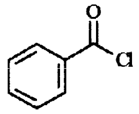
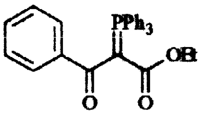
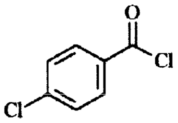
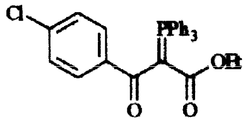
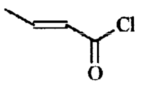
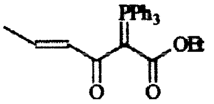
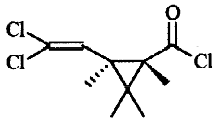
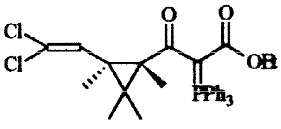
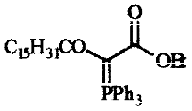
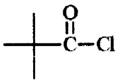
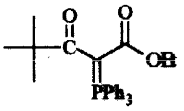
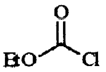
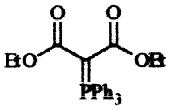
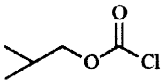
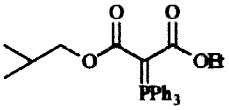
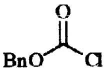
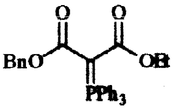
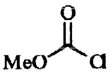
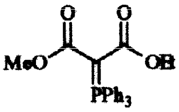
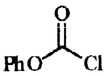
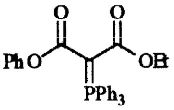
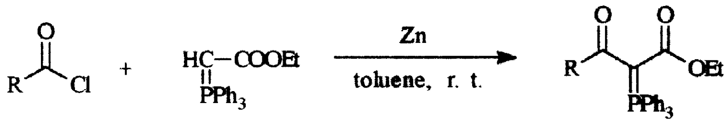
Table-1 : Substitution at α-carbon of ylide

entry	Acid chloride/chloroformate	Product	Time (h.)	Yield (%)[a]
1.	$H_3C{-}COCl$		2	82
2.	$CH_3CH_2{-}COCl$		3	80
3.			2.5	85
4.			3	81
5.			3	80
6.			3	80
7.	$C_{15}H_{31}COCl$		2	81
8.			3	80
9.			2	83
10.			2.5	81
11.			3	85
12.			2.5	80
13.			3	81

a : All the products exhibited physical and spectral (NMR, IR & Mass) properties in accord with the assigned structures our work on zinc catalysed reactions, herein we wish to report a zinc promoted facile acylation of stabilised ylides at the α-carbon.

Scheme



R = alkyl, aryl, cyclopropyl, ethoxy, methoxy, isobutoxy, phenoxy and benzyloxy

The reaction of acid chlorides or chloroformates with ylide is carried out in anhydrous toluene in the presence of zinc (metal grade). The reaction is fast and gives clean products in only a few hours.

Typical procedure; To a solution of acid chloride or chloroformate (10 mmol) in toluene (20 ml), was added activated zinc dust (10 mmol) and the suspension was stirred for 10 minutes. Then a toluene solution of ylide (10 mmol in 20 ml) was added and stirring continued for the given time (see table). The progress of the reaction was monitored by tlc. After completion of the reaction, the mixture was filtered and the solid washed with ether (100 ml). The combined organic layer was washed with $NaHCO_3$ solution (10%, 50 ml), water and dried over Na_2SO_4. Evaporation of the solvent gave the product in good yield and high purity.

Notable features of the procedure are the high yields and the fact that double bond present elsewhere in the molecule remains unaffected. A control experiment reacting acid chloride with ylide in toluene, without zinc does not yield desired acylated product. The efficiency of the reaction can be explained by the fact that the polar groups complex to the surface of zinc, thus increasing the electrophilic character of the acyl groups.[9] The detailed mechanistic aspects of the reaction are under investigation. We have observed that the method has general application (see table) for the preparation of a variety of α-acyl ylides.

In conclusion, we have described a mild, highly efficient and convenient method for the acylation of ylides with a variety of acid chlorides or chloroformates. The use of metal grade zinc powder makes the procedure inexpensive and offers advantages over existing methods. Further studies to determine the scope, limitation and applications of this zinc promoted protocol are under investigation and will be reported in due course.

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