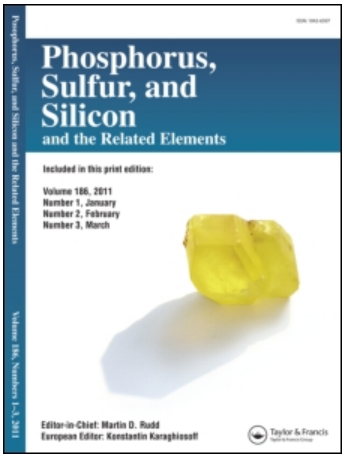

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

AN EFFICIENT PROCEDURE FOR ACETALIZATION OF CARBONYL COMPOUNDS WITH P_2O_5/SiO_2

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Online publication date: 16 August 2010

To cite this Article Mirjalili, Bibi Fatemeh , Zolfigol, Mohammad Ali , Bamoniri, Abdolhamid , Amrollahi, Mohammad Ali and Hazar, Azizeh(2004) 'AN EFFICIENT PROCEDURE FOR ACETALIZATION OF CARBONYL COMPOUNDS WITH P_2O_5/SiO_2', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 7, 1397 — 1401
To link to this Article: DOI: 10.1080/10426500490463583
URL: http://dx.doi.org/10.1080/10426500490463583

Phosphorus, Sulfur, and Silicon, 179:1397–1401, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490463583

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AN EFFICIENT PROCEDURE FOR ACETALIZATION OF CARBONYL COMPOUNDS WITH P_2O_5/SiO_2

Bibi Fatemeh Mirjalili,[a] *Mohammad Ali Zolfigol,*[b] *Abdolhamid Bamoniri,*[c] *Mohammad Ali Amrollahi,*[a] *and Azizeh Hazar*[a]
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(Received October 23, 2003; in final form November 13, 2003)

P_2O_5 as a dehydrating agent can be used for acetalization of carbonyl compounds. This reaction is very fast with high yield and also comparable with acetal formation by using microwave irradiation.

Keywords: Acetalization; dehydrating agent; diphosphorus pentoxide

The carbonyl function, as present in aldehydes and ketones, is the most versatile functional group in organic synthesis. A major problem in a synthesis of any lengths is to shield a carbonyl function from nucleophilic attack until such time as its electrophilic properties must be exploited. One of the most useful protecting methods for carbonyl compounds is acetalization and thioacetalization.[1] Acetals are not only the most widely used protecting groups but are also efficient chiral auxiliary groups for enantioselective synthesis.[2] The most convenient and practical methods for acetalization are reaction of carbonyl compounds with ethylene glycol in the presence of an appropriate catalyst, with removal of water formed polyanillin-supported sulfuric acid,[3] pyridinium salts,[4] $SbCl_3^5$, rhodium, ruthenium and iridium complexes,[6] silica gel supported metallic sulfates,[7] Tungsten hexachloride,[8] zirconium tetrachloride,[9] DDQ,[10] NBS,[11] Envirocat EPZG,[12] hydroxy complexes of palladium(II) and platinium(II),[13] iodine,[14] titanium cation-exchange montmorillonite[15] are usually utilized as catalyst.

Financial support for this work by Research Affairs, Yazd University, Yazd, Iran and Bu-Ali Sina University, Hamadan, Iran, is gratefully acknowledged.

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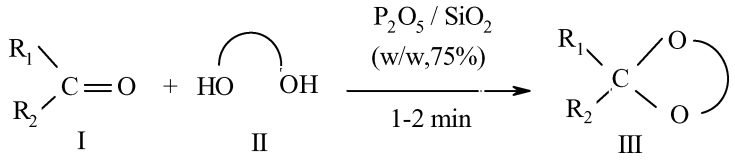
Dehyrating agents such as calcium sulfate, aluminum oxide, copper sulfate and molecular sieve are also used for the acetal formation.[16] Literature survey shows that phosphorus pentoxide (phosphoric anhydride) as a dehydrating agent was used for formation of anhydride from two molecules of an ordinary acid, ketenimine from amide, vinyl ether from acetal, nitrile from amide,[17] amide from oxime,[18] phenolic ester from carboxylic acid[19] and so on. On the basis of the above mentioned ability of P_2O_5 we decided to use it for the acetalization of some diols. Therefore, we have been used silica supported form of P_2O_5 due to advantages which was reported by Eshghi *et al.*[19]

RESULTS AND DISCUSSION

We report herein that acetals and ketals can be prepared very fast and in excellent yields by the direct condensation of any diols with aldehydes/ketones under heterogeneous condition by employing of P_2O_5/SiO_2 (w/w 75%) at room temperature (Scheme 1).



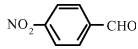
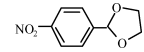
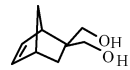
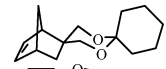
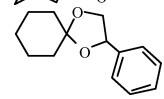
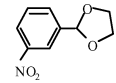
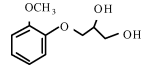
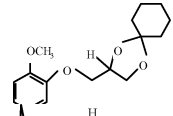
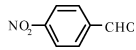
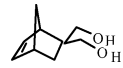
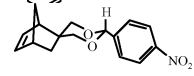
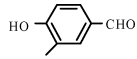
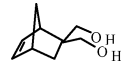
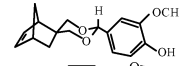
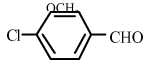
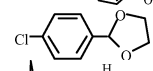
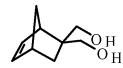
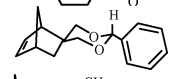
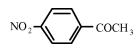
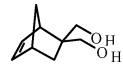
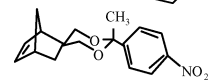
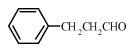
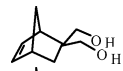
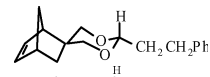
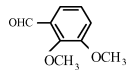
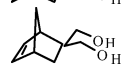
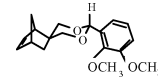
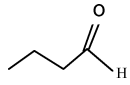
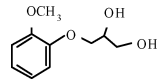
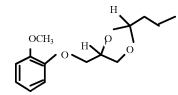
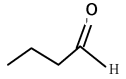
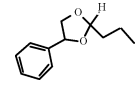
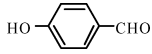
SCHEME 1

Various aldehydes and ketones with different kinds of diols were subjected to acetalization reaction in the presence of P_2O_5/SiO_2 (w/w 75%) (Table 1). Reaction is exothermic, simple and work-up procedures are very easy and convenient. In this procedure, did not need tedious neutralization during work-up and azeotropically removing of water by Dean-stark apparatus. Although for liquid starting materials, did not need a solvent, but for solid materials, acetonirile were used as solvent. This Procedure is very fast and is comparable with acetalization under microwave irradiation.[20,21]

EXPERIMENTAL SECTION

General: Chemicals such as carbonyl compounds, ethylene glycol, phenyl ethylene glycol, guaiacol glyceryl ether, diphosphorus pentoxide, acetonitrile, and silica gel were purchased from Fluka, Merck, and

TABLE I Rapid Acetalization/Ketalization of Aldehydes and Ketones(I) by P_2O_5/ SiO_2 (w/w, 75%) at Room Temperature

Entry	Carbonyl compound (I) (10 mmole)	Diol (II) (10–12 mmole)	Product (III)	Acetonitrile (mL)	P_2O_5/SiO_2 (w/w,75%) (gr)	Yield[a] (%)
1		$HOCH_2$ CH_2OH		—	2	85
2		$HPCH_2$ CH_2OH		—	1.5	90
3				3	2	88
4		PhCHOH-CH_2OH		3	2	84
5		$HOCH_2$ CH_2OH		—	1.5	89
6				3	2	85
7				5	1.5	90
8				5	2	84
9		$HOCH_2$ CH_2OH		—	1.5	90
10				3	2	87
11				5	2	85
12				3	2	83
13				5	2	85
14				3	1.5	88
15		PhCHOH-Ch_2OH		3	1.5	85
16				5	2	82

[a]Isolated yield.

Aldrich chemical companies. 5-Norbornene-2,2-dimethylol was synthesized according to our previously reported procedure.[20] The acetalization products were characterized by comparison of their spectral IR, ^{1}H-NMR, TLC, and physical data with authentic samples.

General Procedure for the Preparation of Acetals or Ketals

To a stirred mixture of carbonyl compound and diol in acetonirile or without solvent was added a mixture of P_2O_5/SiO_2 (w/w75%) rapidly (Table I). The reactions are exothermic and after 1–2 min were completed. The reaction vessel was cooled and the heterogeneous mixture washed with dichloromethane and decanted. After removal of solvent, we worked-up and isolated the pure product.

Preparation of Acetal(7) from 4-Nitro Benzaldehyde. A Typical Procedure

To a stirred and hot mixture of 4-nitrobenzaldehyde(1.51 g, 10 mmol), 5-norbornene 2,2-dimethylol (1.55 g, 10 mmol) and acetonitrile (5 mL), P_2O_5/SiO_2 [(w/w 75%), 1.5 g] were added. Reaction is exothermic and completed after 60 sec. The reaction vessel was cooled and the heterogeneous mixture washed with dichloromethane and then decanted. After removal of solvent, by addition of ethanol and water, the acetal as pure crystal was obtained. Yield: 2.3 g (90%), m.p: 123–125°C. [Lit.[20] m.p.: 124°C]

CONCLUSION

Acetals and ketals can be prepared very fast and in excellent yields by the direct condensation of any diol with aldehydes/ketones under heterogeneous condition by employing P_2O_5/SiO_2 (w/w 75%) at room temperature. The cheapness and availability of the reagent, easy procedure and work-up make this method attractive for the organic chemists.

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