Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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To cite this article: Hossien Eshghi, Mohammad Rafei & Mohammad Hasan Karimi (2001) P_2O_5/SiO_2 AS AN EFFICIENT REAGENT FOR ESTERIFICATION OF PHENOLS IN DRY MEDIA, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:5, 771-774, DOI: 10.1081/SCC-100103268

To link to this article: http://dx.doi.org/10.1081/SCC-100103268

SYNTHETIC COMMUNICATIONS, 31(5), 771–774 (2001)

P_2O_5/SiO_2 AS AN EFFICIENT REAGENT FOR ESTERIFICATION OF PHENOLS IN DRY MEDIA

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ABSTRACT

A simple and efficient method for esterification of carboxylic acid with phenols using P_2O_5/SiO_2 reagent in dry media is reported.

Esters are common intermediates in natural product chemistry due to their stability and accessibility for easy interconversion.[1] It has long been known that the process of esterification may be enormously hastened by the addition of a strong acid, such as sulfuric acid. The classical methods for the synthesis of esters are not suitable for acid sensitive compounds and have the disadvantages of the corrosiveness of strong acid and accompanying side reactions such as carbonization, oxidation, etc. Further modifications of methods have been made with alcohols and carboxylic acids which have some advantages over the classical acid catalyst.[3–5] However acylated phenols are obtained under standard conditions from the phenol and the appropriate acid chloride or anhydride in the presence of a base.[6] The use of acyl esters as phenol protecting groups has found widespread application especially in preparative chemistry.

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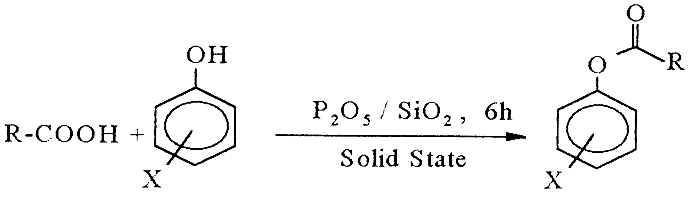
Phosphorous pentoxide has been frequently used in esterification of carboxylic acid by excess alcohol.[7,8] The nature of the species obtained from interaction of P_2O_5 with alcohols is critically dependent upon the stoichiometry of the components. The reagent formed presumably consists of a mixture of alkyl phosphate esters. These organophosphorous reagents have been used for esterification of several primary aliphatic carboxylic acids in varying yields, but the aromatic acids could be recovered unchanged.[8] Coupled with this fact, this solid acidic oxide possessing an extraordinary dehydrating capacity, made itself a unique material of choice for the present investigation.

We herein report a very simple and efficient method for the esterification of carboxylic acids with phenols using the P_2O_5/SiO_2, reagent in dry media. The reagent was prepared by simple mixing of P_2O_5 and dried chromatographic grade silica gel. Stirring of mixture in dry condition for 30 minutes gave the P_2O_5/SiO_2 reagent as homogeneous, free flowing, white powder. This reagent has the advantage of being easily removed from the organic product by filtration. A further advantage of this reagent is improved storage stability in moisture in comparison to P_2O_5, which is very sensitive to moisture.

When the P_2O_5/SiO_2 reagent was mixed with equimolar amounts of the carboxylic acids and phenols, the corresponding esters were obtained in high yields (Table, Scheme). Aliquots of the reagent can be conveniently used for esterification of aliphatic carboxylic acids with phenols by stirring at room temperature for 6 h. The conversion of aromatic carboxylic acids under these conditions, is low (35–60%). The best results were obtained in 65°C, but at higher temperature, Fries rearrangement can occur.[9]



Scheme

The present method is generally applicable to aromatic and aliphatic carboxylic acids and provided the corresponding carboxylic esters in high yield with naphthols and phenols. In all examined cases, the esterification reactions were very clean and led to essentially pure esters. In conclusion, with this readily available reagent, moderate to high yields, mild solvent-free conditions, as well as easy operation, we think that the present work

Table. Esterification of the Carboxylic Acids with Phenols by Using P_2O_5/SiO_2 in Dry Media

				Mp or bp (°C/torr)	
R	X	T/°C	Yield %[a,b]	Found[c]	Reported[ref]
CH_3	H	25	68	195/760	196/760[10]
CH_3	p-CH_3	25	84	210/760	212-213/760[10]
CH_3	m-CH_3	25	72	211/760	212/760[10]
CH_3	p-NO_2	25	65	75–76	76–77.5[11]
CH_3	1-Naphthyl	25	75	46–48	45[10]
CH_3	2-Naphthyl	25	70	69–70	69–70[10]
Ph	H	65	75	69	71[10]
Ph	p-CH_3	65	80	70	71.5[10]
Ph	m-CH_3	65	82	54	55–56[10]
Ph	o-CH_3	65	70	310/760	307/728[12]
Ph	p-NO_2	65	65	142	140–141.5[13]
Ph	1-Naphthyl	65	72	54	56[10]

[a] Isolated yields by column chromatography.
[b] The conversion yields are 70–90%.
[c] The structure of the obtained esters, was confirmed through the ^{1}H-NMR and IR spectra and also by comparison with authentic samples.

described herein provides a useful method for esterification of the carboxylic acids with naphthols and phenols. Further studies of the new applications of P_2O_5/SiO_2 in organic synthesis are under way.

EXPERIMENTAL SECTION

All melting points recorded are uncorrected open capillary measurements. Infrared spectra were recorded on a Shimadzu-IR 470 spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker-80 MHz instrument using tetramethylsilane (TMS) as internal standard. The silica gel 60 was obtained from E Merck and dried in an oven at 120°C 2 h.

General Esterification Procedures: A mixture of 1.42 g (0.01 mol) phosphorus pentoxide and 2.5 g of chromatography grade silica gel was placed in a flask and stirred for 30 minutes. A mixture of equimolar amounts (5 mmol) of the carboxylic acid and phenol was added. Usually an immediate color change was observed. After stirring for 6 h at the temperature which indicated in the Table, methylene chloride (50 ml) was added. The mixture was stirred for 1 minute and then filtered. The spent reagent was washed twice with methylene chloride (10 ml). The combined organics were washed with aqueous NaOH solution, water, and dried over sodium sulphate, and the solvent was removed under reduced pressure.

This crude reaction mixture was analysed and purified in a conventional manner. The esters (Table) were identified by comparison of the ^{1}H-NMR and IR spectra with authentic samples.

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Received in the U.K. December 20, 1999