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Short communication

SHORT COMMUNICATION

The use of pyridinium fluorochromate (PFC) supported on TriSyl silica gel for oxidation reactions

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Abstract: Pyridinium fluorochromate supported on TriSyl silicas was prepared by co-adsorption. The supported reagent was used in equimolar quantity to oxidise some organic compounds with good yields and complete selectivity. These procedures are mild, efficient, safe and the work-ups are very convenient.

Keywords: oxidation, pyridinium fluorochromate (PFC), TriSyl silicas.

INTRODUCTION

Oxidation is an important process in organic synthesis and a wide range of compounds have actually been employed to carry out this reaction. Chromic acid[1] and chromium(VI) based reagents are versatile oxidising agents and typical reagents based on chromium(VI) are the Jones, Sarett, Collins reagents, *etc.*[2] In recent times, the oxidation of alcohols using catalytic systems has been carried out,[3–5] while the utility of chromium oxidants has been reduced due to their hazardous toxicity, the potential danger in handling chromium compounds, disposal problems and work-up difficulties in product isolation.

The introduction of supported reagents has produced an attractive option for organic synthesis. These reagents not only modify the activity but may also import specific product selectivity.[6] They also reduce difficulties in product isolation. A large number of supported chromium (VI) oxidants have been reported.[7–9] However, there is still scope to develop a reagent which has an easy method of preparation, a longer shelf life without any special conditions of storage and better activity.

TriSyl is the commercial name of silica gel produced under carefully controlled conditions in order to achieve specific adsorbing properties. It is known that TriSyl silicas are selective and highly efficient adsorbent of phosphatides, trace metals (notably copper and iron), soap and oxidation compounds from glyceride

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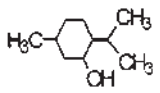
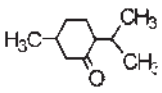
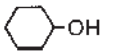
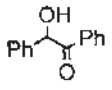
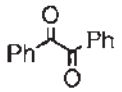
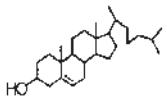
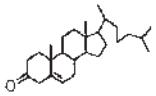
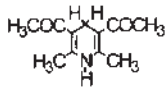
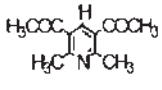
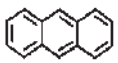
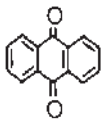
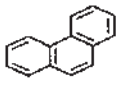
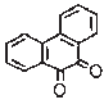
TABLE I. Yields of oxidation products using PFC/TriSyl reagent[i,ii]

No	Substrate[a]	Product[b]	PFC/TriSyl			PFC (Lit.12-13)		
			Substrate/ Oxidant mol/mol	Time h	Yield %	Substrate / Oxidant mol/mol	Time h	Yield %
1	C_4H_9OH	C_3H_7CHO	1/1	1.0	93	1/ 1.5	2.0	94
2	$PhCH_2OH$	PhCHO	1/1	0.5	90	1/ 1.25	0.75	90
3			1/1	1.0	80	1/2.0	6.0	96
4			1/1	2.5	92	1/1.5	3.5	89
5			1/1	1.5	95	1/1.5	2.5	98
6			1/1	1.0	81	1/2.0	6.0	96
7			1/1	0.5	90	-	-	-
8	PhSH	Ph-S-S-Ph	1/1	0.5	73	-	-	-
9			1/1	1.5	90	1/ 2.5	4.0	98
10			1/1	0.5	80	1/ 2.5	5.0	52

i: All reactions were carried out at room temp. in dichloromethane, *ii*: The products were characterised by comparision with authentic samples, ^{1}H-NMR, FT-IR and m.p. measurements (except for benzaldehyde, butanal, menthone and cyclohexanone; they were identified as 2,4-dinitrophenylhydrazone derivatives)

oils in the edible oil refining industry,[10] and also they are used to remove water-soluble cationic dyes from dye contamined water.[11]

Herein, a TriSyl supported pyridinium fluorochromate (PFC) reagent for the oxidation of alcohols and some other organic substances is reported.

EXPERIMENTAL

Preparation of the PFC-TriSyl silica gel reagent. TriSyl silica was obtained from Grace Speciality Chemical Co. (Germany).[10] Pyridinium fluorochromate, $C_5H_5NHCrO_3F$ (PFC) was synthesised and recrystallised by the method decribed elsewhere.[12] PFC (20 g, 100 mmol) was dissolved in acetone (50 mL) and TriSyl (40 g) was then added under stirring at 25 °C for 15 min. The excess solvent was evaporated under reduced pressure using a rotary evaporator. The yellow-orange powder solid was dried in a vacuum desiccator. PFC/TriSyl can be stored for at least 2 months in air and at room temperature without losing its activity.

Typical oxidation procedure. Benzoin (**5a**) (2.11 g, 10 mmol) was disolved in dichloromethane (15 mL) and added dropwise on to PFC/TriSyl (6 g, PFC content 10 mmol) in a round-bottom flask. The heterogeneous mixture was magnetically stirred for the described reaction time. The progress of the reaction was followed by TLC (solvent hexane/ethyl acetate, 90/10, v/v). After completion of the reaction, the mixture which had been converted to black granules was filtered through a sintered glass filter and the residue was washed with hot dichloromethane. The excess solvent was evaporated from the combined filtrates using a rotary evaporator. Column chromatography of the residue using ethyl acetate:hexane (1:4) afforded benzil (**5b**) (2 g, 95%), m.p. 96 °C (Lit. 95–96 °C). IR and ^{1}H-NMR spectra were confirmed with authentic material.

The results of the oxidation studies using the PFC/TriSyl reagent are summarised in Table I.

RESULTS AND DISCUSSION

Water was not used when physisorbed preparing the reagent because TriSyl silica has hydrogel properties. The preparation of the physisorbed reagent of TriSyl silica gel supported pyridinium fluorochromate (PFC) is quite straightforward. The physisorbed reagent shows better shelf life for long periods without decomposition compared to PFC. It is converted in an equimolar quantity for the oxidation of primary, secondary and benzylic alcohols to the corresponding carbonyl compounds, of polycyclic arenes to quinones, of an Δ^5-steroid to the unsaturated ketone, of a thiol to disulfide and of a 1,4-DHP to pyridine derivative in good yields.

PFC is known as a chromium based reagent, but black gums occur in the reaction media during the oxidation. Isolation of the product from the black gums is fairly difficult. However, after oxidation with TriSyl supported PFC, black granules are formed in the reaction medium. Therefore, working with the physisorbed reagent is easier than working with PFC itself as for the isolation of the product, procedures such as filtration and extraction can be employed because the reduced chromium was adsorbed on the TriSyl silica gel. Furthermore, compared to other studies,[12,13] better yields were obtained according to the reaction time and spent oxidant equivalent.

ИЗВОД

ПРИМЕНА ПИРИДИНИЈУМ-ФЛУОРОХРОМАТА (PFC) НАНЕТОГ НА TriSyl СИЛИКАГЕЛ У РЕАКЦИЈАМА ОКСИДАЦИЈЕ

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Пиридинијум-флуорохромат нанет на TriSyl силикагел припремљен је ко-адсорпцијом. Реагенси су коришћени у еквимоларним количинама за оксидацију неких органских једињења са добрим приносом и комплетном селективношћу. Поступак је благ, ефикасан, безбедан и лако се изводи.

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