

NOTE

***N*-(4-Pyridinium dichromate)-*p*-Toluenesulphonamide as an Efficient Oxidant for Alcohols Under Mild Condition**

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N-(4-Pyridinium dichromate)-*p*-toluenesulphonamide [NPDS] when reacted with alcohols and converts them to their corresponding carbonyl compounds in good yields under mild conditions.

Key Words: Synthesis, Reagent, Oxidation, Alcohols.

The selective oxidation of primary and secondary alcohols to their corresponding aldehydes and ketones, respectively, plays a pivotal role in synthetic-organic chemistry.^{1,2} A great variety of compounds containing chromium(VI) have proved to be versatile reagents capable of oxidizing almost every oxidizable organic functional group³⁻⁵. The oxidation of organic substrates may occur by chromium(VI) reagents in aqueous solution under acidic or neutral conditions and in some cases with the aid of co-solvents which help to dissolve the organic substrates. However, in almost all of these cases the pH of the reaction medium and the presence of water-forming hydrolytic reaction exclude the use of this reagent for oxidation of molecules containing groups sensitive to acid or water. Therefore, oxidation reactions in organic media have been of great importance in modern organic synthesis. For this purpose and also to improve the selectivity of oxidation and the mildness of reaction conditions, in recent decades a number of oxochromium-amine complexes have been developed and reported in the literature.⁶ An important class of such complexes is amine dichromates which have found wide application in many types of oxidative transformations. The first of such reagents was pyridinium dichromate, reported by Corey and Schmidt⁷, which exhibited great oxidation efficiency in solvents such as methylene chloride and dimethyl formamide. Other reported amine dichromate reagents are nicotinium dichromate⁸, quinolinium dichromate⁹, bis-tetrabutylammonium dichromate¹⁰, and pyrazinium dichromate¹¹. Polymeric analogue of some of these reagents has also been reported in the literature¹². Almost all of these reagents are capable of oxidizing different types of alcohols and many other substrates; however, some of the reagents reported for oxidation of different alcohols are often high acidity, no selectivity, hygroscopicity, photosensitivity, tedious work-up procedures,

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ignition during preparation, and cost of preparation. Thus, a milder, selective, non-hazardous and inexpensive reagent is still in demand.

We now report a convenient method for the oxidation of alcohols to their corresponding carbonyl compounds using *N*-(4-pyridinium dichromate)-*p*-toluenesulphonamide. (NPPTS) **2** that was prepared from *N*-(4-pyridyl)-*p*-toluenesulphonamide [**1**] (Fig. 1).

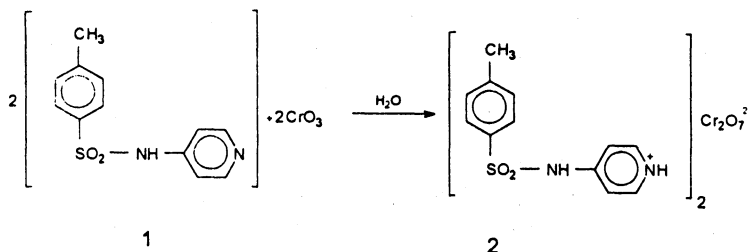
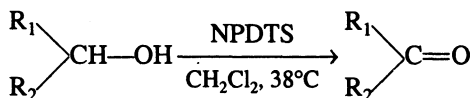


Fig. 1

The reaction of alcohols with NPPTS in CH_2Cl_2 afforded carbonyl compounds without side products (Scheme-1).



Scheme-1

N-(4-Pyridinium dichromate)-*p*-toluenesulphonamide was easily prepared in a good yield by addition of a suspension of *N*-(4-pyridyl)-*p*-toluenesulphonamide in water to a cold solution of CrO_3 in a correspondingly minimum amount of water. This orange coloured oxidizing agent is a stable compound and can be stored for months without losing its activity. It is not hygroscopic or light sensitive. The presence of the dichromate anion in the reagent was confirmed by IR spectrum having bands at 930 and 765 cm^{-1} characteristics for the dichromate anion¹³.

TABLE-1
OXIDATION OF DIFFERENT ALCOHOLS WITH NPPTS

Entry	Alcohol	Product	Molar ratio	Reaction time (h)	Yield (%)
1.	Benzyl alcohol	Benzaldehyde	2 : 1	2	95
2.	1-Butanol	Butanal	2 : 1	8.5	90
3.	2-Butanol	2-Butanone	2 : 1	10	90
4.	1-Pentanol	Pentanal	2 : 1	9	87
5.	1-Hexanol	Hexanal	2 : 1	10	82
6.	2-Hexanol	2-Hexanone	2 : 1	8	90
7.	1-Heptanol	Heptanal	2 : 1	12	80
8.	1-Octanol	Octanal	2 : 1	12	90
9.	Cyclopentanol	Cyclopentanone	2 : 1	13	85
10.	Cyclohexanol	Cyclohexanone	2 : 1	12	85

As shown in Table-1, benzyl and other saturated alcohols were oxidized to their corresponding aldehydes and ketones with *N*-(4-pyridinium dichromate)-*p*-toluenesulphonamide in CH_2Cl_2 at 38°C . Further oxidation of products was not observed. In conclusion, the mildness, stability, nonhygroscopicity, high efficiency and reasonable reaction time of this reagent make it a useful addition to the several reported chromium(VI) based oxidants for the oxidation of different alcohols.

Preparation of *N*-(4-pyridinium dichromate)-*p*-toluenesulphonamide

To a suspension of 0.05 mol (12.4 g) of *N*-(4-pyridyl)-*p*-toluenesulphonamide in 50 mL water in a 100 mL flask was added a cold solution of 0.06 mol of CrO_3 in 5 mL of water. Formation of the reagent occurred very smoothly. No heat was evolved during the stirring of reaction mixture. After filtration, the reagent was washed repeatedly with 30 mL of water until the filtrate was colorless. In general the reagent was used without drying.

General procedure for oxidation of alcohols is as follows:

The general procedure involved reaction of 6 mmol (4.28 g) of reagent with 3 mmol of alcohol in 20 mL of CH_2Cl_2 at 38°C . The progress of the reactions was monitored by TLC. After completion of reaction the products could be obtained in the soluble phase by filtering the reagent and washing it with 20 mL portions of diethyl ether.

The combined solution was washed with dilute hydrochloric acid, sodium bicarbonate solution and water to remove the residual amount of chromium salts. Removal of the solvent gave the crude product; it was dissolved in diethyl ether. Ether solution was dried and concentrated. The product was identified by IR and NMR spectral studies.

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