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A new oxidative reagent synthesis and its applications: *Tetrakis*-(2,4,6-trimethylpyridine)silver(I) dichromate (T-TMPSDC)

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ABSTRACT

Tetrakis-(2,4,6-trimethylpyridine)silver(I) dichromate (T-TMPSDC) was easily synthesized by addition of 2,4,6-trimethylpyridine to an aqueous precipitation of silver dichromate and characterized thoroughly, using spectroscopic and others analytical methods such as FT-IR, ^{1}H NMR, ^{13}C NMR, DTA, SEM-EDS and XRD. When T-TMPSDC was used as an oxidative reagent, it showed selectivity in the oxidation of primary, secondary and benzylic alcohols to their corresponding carbonyl compounds in presence of benzylic carbons and arenes such as tetraline, anthracene and phenanthrene.

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1. Introduction

The oxidation of organic compounds is very important not only in living systems in general but also specifically in analytical chemistry, synthetic chemistry and many other industrial areas. The oxidation of compounds occurs by alteration of the functional group. The limitation of this changing is defined as selective oxidation. Both oxidative reagents and solvent used in the experimental stages are very important in the selective oxidation of organic compounds. For this purpose, the synthesis of oxidative reagents used in aprotic reaction conditions has been increasing recently [1-3]. These reagents based on the oxochromic-amine complex are widely used in applications of many oxidative reactions such as pyridinium chlorochromate [4], pyridinium fluorochromate [5], pyridinium dichromate [6], 3-carboxypyridinium trichloro acetatechromate [7] and *tetrakis*-pyridinium silver(I) dichromate [8]. Generally, these are known as hexavalent chromium reagents [9-17].

In this study, a new oxidative reagent, *tetrakis*(2,4,6-trimethylpyridine)silver(I) dichromate was synthesized by adding 2,4,6-trimethylpyridine on silver dichromate made up of silver nitrate and potassium dichromate. The structure of the compound was confirmed on basis of FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopic methods. Its morphology and structural characterization were examined using energy-dispersive X-ray spectrometry which is integrated in scanning electron microscopy (SEM-EDX) and X-ray diffraction (XRD) spectroscopic methods. The compound was used for the oxidation of various alcohols by changing solvent conditions. It was also tested for the oxidation of allylic, benzylic carbons and arenes.

2. Experimental

2.1. Materials and analysis

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE DPX NMR spectrometer operating at 400.2 and 101.6 MHz.

Infrared absorption spectra were obtained from a Perkin Elmer BX II spectrometer and were reported in cm^{-1} units.

Melting points were measured on an Electro Thermal IA 9100 apparatus using a capillary tube.

It were used Setaram LABSYS Evo 1600 was used for DTA/TG analysis and a PANalytical X'Pert Pro MPD diffractometer was used for XRD.

SEM images and EDS spectra were obtained from JEOL FE-SEM:JSM-7100F-EDX spectrometer.

All chemicals were purchased from Merck and Aldrich.

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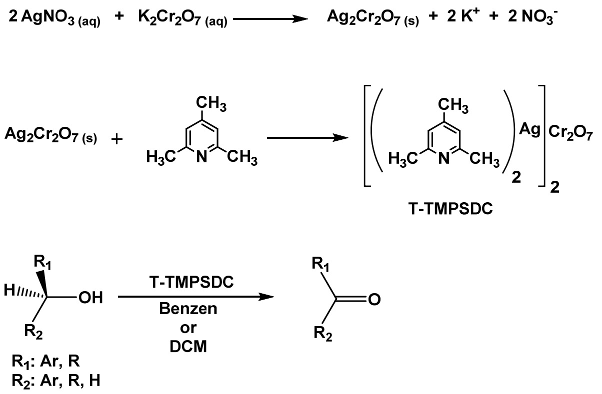

Scheme 1

2.2. Preparation of tetrakis-(2,4,6-trimethylpyridine) silver(I) dichromate reagent

Potassium dichromate (0.743 g, 2.5 mmol) in distilled water (15 mL) was added by stirring to solution of silver(I) nitrate (0.850 g, 5.0 mmol) in distilled water (15 mL). After then, 2,4,6-trimethylpyridine (1.210 g, 10 mmol) was added dropwise without filtration onto the obtained silver dichromate ($Ag_2Cr_2O_7$) in the aqueous medium, with magnetic stirring at 50 °C for 15 min. Upon completion of the reaction, the precipitate was filtered and washed with water. The yellow-orange powder solid was dried in a vacuum desiccator (Scheme 1). T-TMPSDC can be preserved for at least six months in air and at room temperature without losing its activity. Yield: 70%. M.p.: 195-196 °C. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.13 (s, 2H, C-$H_{arom.}$), 2.30 (s, 6H, *o*-CH_3), 3.40 (s, 3H, *p*-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 20.3 (CH_3), 25.5 (CH_3), 157.1, 149.8, 122.2 ($C_{arom.}$). FT-IR (ν, cm^{-1}): 3055 (C-$H_{arom.}$), 2987 (C-$H_{aliphatic}$), 1618 (C=$N_{pyridine}$), 1463 (C=$C_{arom.}$), 920 (Cr=O), 768 (Cr-O).

2.3. Typical oxidation procedure

Benzyl alcohol (**1a**) (0.54 g, 5 mmol) was dissolved in dichloromethane (15 mL) and added dropwise on to T-TMPSDC (4.57 g, 5 mmol) in 15 mL dichloromethane in a round-bottom flask. The heterogeneous mixture was magnetically stirred under reflux conditions for 1 hour. The progress of the reaction was monitored by T.L.C. (solvent; 50:50 hexane:ethyl acetate, *v*:*v*). Upon completion of the reaction, brown-black granule was filtered by a sintered glass funnel and the residue was washed with hot dichloromethane. After the excess solvent was removed using a rotary evaporator, the residue was purified by short column chromatography on silica gel using ethyl acetate:hexane (2:1, *v*:*v*) as eluant. The conversion of functional group was monitored with FT-IR spectral analysis. Benzaldehyde **1b** was obtained with 85% yield. The product formed was also analyzed by its 2,4-dinitrophenylhydrazone (2,4-DNP). The precipitated 2,4-DNP was filtered off, weighed and recrystallized from ethanol. M.p.: 237 °C [Lit. 237 °C] [18]

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Thermal property analysis

The technique of differential thermal analysis (DTA) has provided much information about physical and chemical changes in material such as T-TMPSDC when is heated. In this study, the thermal stability of T-TMPSDC was tested by heating between 0-1000 °C at a heating rate of 10 °C/min in nitrogen atmosphere using TG-DTA analysis. DTA and TG curves show that the main decomposition can be noted at temperatures around 123 and 195 °C involving 51.91% mass loss and below 105 °C, which corresponds to the lattice water molecules (calculated, 3.64%). By following calculations; it is confirmed that it has coordinated with four units from TGA analysis data as 2,4,6-trimethylpyridine ($C_8H_{11}N$, 121 g/mol) and *tetrakis*-(2,4,6-trimethylpyridine)silver(I) dichromate ($C_{32}H_{44}Ag_2Cr_2N_4O_7$, 914 g/mol). Theoretical and experimental calculations (52.9%, 51.91%, respectively) of organic unit of the compound have verified that it is coordinated with four units of 2,4,6-trimethylpyridine.

3.1.2. SEM and EDS analysis of T-TMPSDC

Firstly, the morphology and size of T-TMPSDC was investigated using SEM technique. The images showed that the samples are of similar morphological and different sized sheet-crystal types in Figure 1a. The SEM images of T-TMPSDC and used are displayed in Figure 1a and b, respectively.

Secondly, Energy-Dispersive X-ray Spectrometry (EDS) was performed in order to determine chemical composition of T-TPMSDC. From the EDS spectrum (Figure 1c), Ag, Cr, O, C and N elements were detected, which probably resulted from the structure of the reagent. The presence of carbon and nitrogen elements in this spectrum is because the $Ag_2Cr_2O_7$ is capped by 2,4,6-trimethylpyridine. In addition, the XRD spectrum of the sample was investigated by using a 40 kV 30 mA Cu cathode, X'celerator detector, recycle 0.02 step size, ¼ divergence slit, antiscatter slit between 3-70°2q. It showed similar properties for $Ag_2Cr_2O_7$ nanoparticles [19,20].

3.1.3. Spectral analysis

FT-IR and NMR spectroscopic techniques were used to identify the synthesized material. The presence of carbon, nitrogen and oxygen elements in this spectrum is because the $Ag_2Cr_2O_7$ is capped by 2,4,6-trimethylpyridine. Figure 2 shows the FT-IR spectrum of the sample in the range 650-4000 cm^{-1}. The FT-IR spectrum showed absorption band regions at 3055, 2987 and 1618 cm^{-1} due to aromatic C-H, aliphatic C-H (methyl groups) and aromatic C=N groups, respectively. The FT-IR spectrum of $Ag_2Cr_2O_7$ obtained from the sample showed strong absorption band at 920 and 768 cm^{-1} which may be due to the vibration modes of Cr=O and Cr-O, respectively.

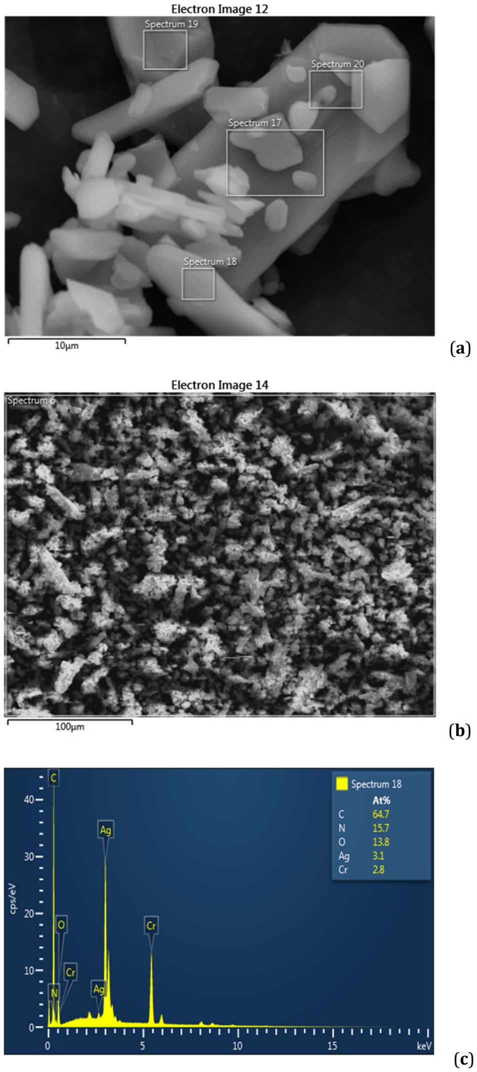

Figure 1. SEM images of reagent (a) and used reagent (b), EDS spectrum of reagent (T-TMPSDC) (c).

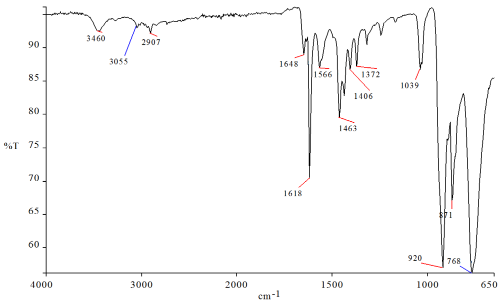

Figure 2. FT-IR Spectrum of T-TMPSDC.

In the ^{1}H NMR spectrum (Figure 3a), the singlet peak observed at δ 7.13 ppm is due to two hydrogen atoms being present in the pyridine ring. The singlets observed at δ 2.30 and 2.60 ppm are due to six and three hydrogen atoms of C-CH$_3$ connections of pyridine ring, respectively. On the other hand, in the ^{13}C NMR spectrum (Figure 3b) the signals observed at δ 25.5 and 20.3 ppm indicate the presence of methyl carbons in the pyridine ring. The substituted pyridine ring carbons were observed at δ 157.1, 149.8 and 122.2 ppm.

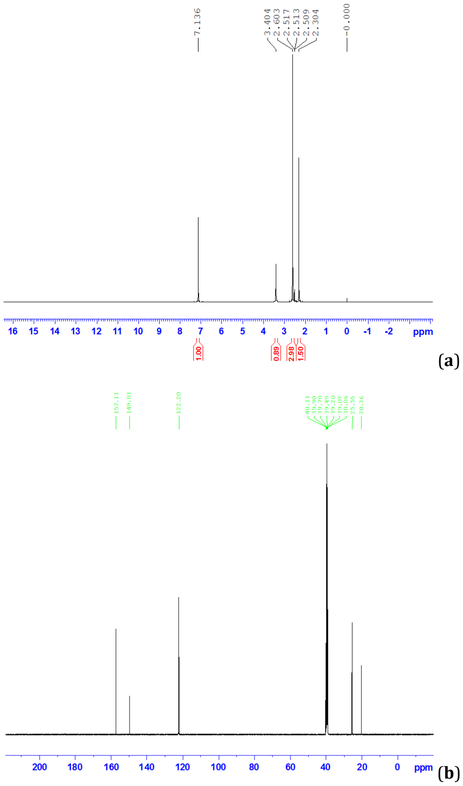

Figure 3. (a) The ^{1}H NMR, (b) ^{13}C NMR spectrums of T-TMPSDC.

3.2. Catalytic activity

A variety of benzyl alcohol derivatives, allylic, primary and secondary aliphatic alcohols were also converted into the corresponding aldehydes and ketones, using the oxidative reagent T-TMPSDC in benzene and dichloromethane, respectively. To show the chemoselectivity of the described system, cinnamyl alcohol was converted to the cinnamaldehyde with high yield and a carbon-carbon double bond was intact in the course of the reaction (Table 1, entry 7b).

In all cases, no over-oxidation products, benzylic carbon and arenes such as tetraline and anthracene and phenanthrene, respectively, were observed even after extended reaction times. Although 1-indanole has both benzylic carbon and benzylic alcohol functional groups, it seems that only alcohol functional group is oxidized to one carbonyl group from spectroscopic data such as FT-IR, ^{1}H NMR and ^{13}C NMR spectrums (Table 1, entry 8b). The results are shown in Table 1, entries 1-16.

4. Conclusion

In summary, T-TMPSDC is a new oxidizing reagent, consisting of chromium(VI) based on the oxochromic-amine complex for the oxidation of the various alcohols to carbonyl compounds is reported. It is easily prepared at high yield and can be dissolved in apolar solvents such as benzene and DCM. It is also selective for the oxidation of primary, secondary and benzylic alcohol in the presence of the benzylic, allylic and arene carbons.

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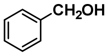
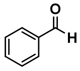
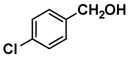
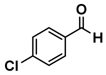
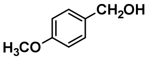
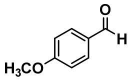
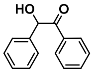
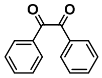
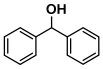
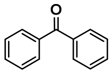
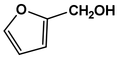
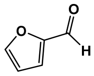
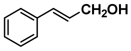
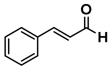
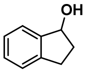
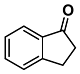
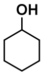
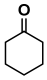
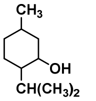
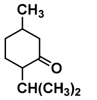
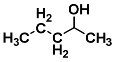
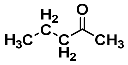
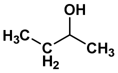
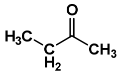
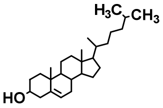
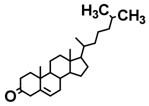
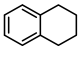
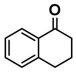
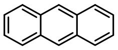
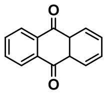
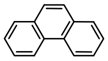
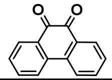
Table 1. Yields of the oxidation products [1,2].

No	Substrate (a)	Product (b)	Solvent				2,4-DNP derivative M.p. °C (Lit.) [18]
			DCM		Benzene		
			Time (h)	Yield (%)	Time (h)	Yield (%)	
1			1	85	1	94	237 (237)
2			1	63	1	88	254 (254)
3			2	77	1.5	92	253 (254)
4			1	60	1	87	-
5			1	82	1	87	240 (239)
6			1.5	64	1.5	89	229 (230)
7			1.5	78	1	90	255 (Dec.)
8			1.5	70	1.5	88	-
9			2	85	1.5	90	160 (162)
10			1.5	45	1.5	83	147 (146)
11			0.5	80	0.5	92	144 (144)
12			0.5	82	0.5	90	118 (117)
13			2.5	65	2.5	84	-
14			6	ND	6	ND	-
15			7	ND	7	ND	-
16			7	ND	7	ND	-

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[1] All reactions were carried out in dichloromethane and benzene.

[2] FT-IR spectrums of all products were identified by comparing with those of authentic samples. Yields were based on 2,4-dinitrophenylhydrazone derivatives identified by melting point (except for benzil (95 °C), indan-1-one (38-40 °C) and 5-cholesten-3-one (125-127 °C) whose melting points were taken directly) [18].

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