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Synthesis and Characterization of a New Oxidation Reagent: Tetrahexylammonium Chlorochromate, $(C_6H_{13})_4N[CrO_3Cl]$

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Abstract. Tetrahexylammonium chlorochromate, THACC, is a new compound, more efficient, and has certain advantages over similar oxidizing agents, in terms of the amount of oxidant, short reaction times, and high yields. This reagent is suitable for oxidizing various primary and secondary alcohols to their corresponding carbonyl compounds**.** The facile oxidation of triphenylphosphine to triphenylphosphine oxide by this reagent in acetonitrile provides a clear-cut example indicating an oxygen atom transfer mechanism**.**

Key words: Chromium(VI), Tetrahexylammonium chlorochromates, Oxidation, Organic substrate, Alcohols.

Resumen. Clorocromato de tetrahexilamonio, THACC, es un nuevo compuesto, más eficiente, y tiene ciertas ventajas sobre agentes oxidantes similares, en términos de la cantidad del oxidante, tiempos de reacción más cortos y elevados rendimientos. Este reactivo es capaz de oxidar varios alcoholes primarios y secundarios a los compuestos carbonílicos correspondientes. La fácil oxidación de trifenilfosfina al óxido de trifenilfosfina por parte de este reactivo en acetonitrilo proporciona un ejemplo de mecanismo de transferencia de átomo de oxígeno.

Palabras clave: Cromo(VI), clorocromatos tetrahexilamónicos, oxidación, substrato orgánico, alcoholes.

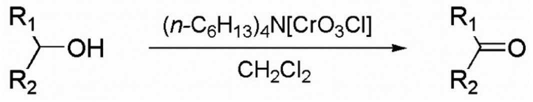
Introduction

Chromium(VI) is established as a versatile oxidant for many types of substrates varying from metal ions to naturally occurring organic compounds, and has a wide range of applications spanning the synthesis of sulfur nanoparticles [1] and the determination of biological oxygen demand in organic polluted water. Cr(VI) as chromate or dichromate is highly soluble in water, and is reported to be highly toxic [2], there are continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions Therefore**,** the search for new oxidizing agents are of interests to synthetic organic chemists. Many such reagents have been developed in recent years with some success [3], some of the important entries in the list of reagents are Pyridinium fluorochromate (PFC) [4] caffeinilium chlorochromate [5], quinolinium fluorochromate [6] triphenylmethylposphonium chlorochromate [7], pyridinium dichromate (PDC) [8] quinolinium chlorochromate, [9] isoquinolinium chlorochromate [10], chromium trioxide-3,5-Dimethylpyrazole complex (CrO_3 3,5-DMP) [11] tributylammonium chlorochromate (TriBACC) [12] prolinium chlorochromate [13], tripropylammonium fluorochromate [14]. In aqueous solutions primary alcohols are usually oxidized to carboxylic acids [15, 16], while in the absence of water the oxidation will stop at the aldehyde. Tetrahexylammonium chlorochromate is more efficient and stronger oxidizing agent. Further, this new compound does not react with acetonitrile, which is suitable medium for studying kinetics and mechanism. There were some primary incentives for selection of $(Hex)_4N^+$ as the counter ion in the work reported in this manuscript. First, quaternary ions such as ammonium are often used as phase transfer catalysts, perhaps making tetrahexylammonium chlorochromate(VI), $(Hex)_4N[CrO_3Cl]$, THACC, a more efficient and stronger oxidizing agent. This new compound is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields. Second, quaternary ions such as ammonium are used as crystal growing agents. Hence, using this counter ion improves the quality of the THACC crystals.

Results and Discussion

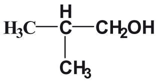
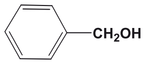
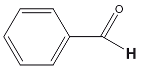
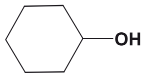
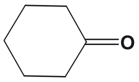
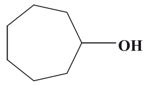
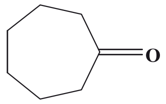
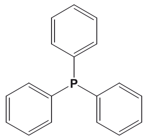
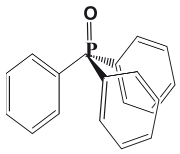
Oxidations of primary alcohols to aldehydes without further oxidation to carboxylic acids is difficult to accomplish with oxidizing agents in aqueous solution because small mounts of aldehyde hydrates, which are in equilibrium with the aldehyde, are readily oxidized to the corresponding carboxylic acids.

Following up on our investigation of chlorochromates (VI) [17, 18], in these manuscripts we are reporting the synthesis of tetrahexylammonium chlorochromate (VI), THACC. The results obtained with THACC are very satisfactory and shows that this new reagent as valuable additions to the existing oxidizing agents. THACC in dichloromethane oxidize primary and secondary alcohols to the corresponding aldehydes or ketones in high yields (Scheme 1, Table 1).

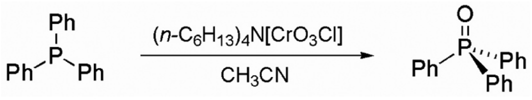


Scheme 1.

Table 1. Oxidations with THACC.

	Substrate	Substrate /Oxidant Ratio	Time (min)		Product	Yield (%)	M.P.(°C)	B.P. (°C)
1a	n-C_3H_7-OH	1/1	123	**2a**	n-C_2H_5-CHO	88		48-50
1b	n-C_4H_9-OH	1/1	95	**2b**	n-C_3H_7-CHO	86		74-75
1c	n-C_5H_{11}-OH	1/1	80	**2c**	n-C_4H_9-CHO	82		102
1d	n-C_6H_{13}-OH	1/1	95	**2d**	n-C_5H_{11}-CHO	92		129-131
1e	 $H_3C-\overset{H}{C}(CH_3)-CH_2OH$	1/1	63	**2e**	$(Me)_2CHCHO$	89		63-64
1f	n-C_8H_{17}-OH	1/1	90	**2f**	n-C_7H_{15}-CHO	85		170-172
1g	n-$C_{11}H_{23}$-OH	1/1	56	**2g**	n-$C_{10}H_{21}$-CHO	87		110-113
1h		1/1	40	**2h**		93		177-179
3a	2-C_3H_7-OH	1/1	105	**4a**	2-C_3H_6O	89		55-57
3b	3-C_7H_{15}-OH	1/1	134	**4b**	3-$C_7H_{14}O$	85		146-148
3c	2-C_4H_9-OH	1/1	90	**4c**	2-C_4H_8O	88		172-173
3d	2-$C_{11}H_{23}$-OH	1/1	78	**4d**	2-$C_{11}H_{22}O$	91		230-234
3e		1/1	185	**4e**		92		154-156
3f		1/1	156	**4f**		82		179-181
3g		1/1.1	4	**4g**		90	156-157	

The reaction of triphenylphosphine with THACC in acetonitrile was carried out at room temperature and triphenylphosphine oxide was obtained in quantitative yields. This provide clear-cut example of oxygen transfer reaction involving THACC and the result may also be useful in defining other related reactions (Scheme 2).



Scheme 2.

The selectivity of THACC is well demonstrated through its oxidations of benzyl alcohol (yield of product: 96%), in the presence of equimolar amounts of 2-phenylethyl alcohol (no product detected). Neither carboxylic acids overoxidation products nor other by-products are formed upon oxidation of alcohols *via* THACC (Table 1). Functional groups such as methoxy and methyl attached on the phenyl ring are inert to this reagent. In addition, we have shown that this reagent does not oxidize a variety of other substrates, including diphenyl sulfide, thiophenol, 3,5-dimethoxyphenol, 2-benzyl-3,4-dihydro-2Hpyran, benzyloxytrimethylsilane, *N*-methyl-2-phenylthioacetamide and sodium 2-hydroxyiminomalonate.

Because of the stability and solubility of tetrahexylammonium chlorochromate reactions could be performed at room temperature and the separation of the products are facile. The chromium(VI) content may be easily determined iodometrically. The IR spectrum of THACC is similar to those of other chlorochromates [19]. This reagent is easy to handle, could be weighed and have no hazardous effect. It is less soluble in dichloromethane and only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

Experimental

Melting points were obtained on an Electrothermal 9100 apparatus. IR spectra were recorded using a Shimadzu IR-420 spectrometer. NMR spectra: ^{1}H and ^{13}C NMR spectra were recorded using Bruker AVANCE DRX-500 in $CDCl_3$ solutions. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. All separations and quantization of alcohols and aldehydes were performed using a Philips 4410 gas Chromatograph. All reagents and solvents are of reagent grades. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ^{1}H and ^{13}C NMR spectra were referenced to external $SiMe_4$. Chromium was estimated iodometrically. In the case of the reduced product of the oxidants, chromium was determined after oxidizing with acidic potassium peroxodisulfate ($K_2S_2O_8$) solution. The percent composition of elements was obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Preparation of tetrahexylammonium chlorochromate, (THACC), $C_{24}H_{52}ClCrNO_3$

To a solution of 1g (0.01 mol) CrO_3 in 25 ml water, placed in a 100 ml beaker and stirring was continued for 0.5 h at 0 °C. Tetrahexylammonium chloride (3.9 g, 10 mmol) was added portion-wise, with stirring. A reddish orange solid is separated and stored in the refrigerator. The solid was washed with hexane and dried under vacuum for 1 h, mp 145 °C. $C_{24}H_{52}ClCrNO_3$: C, 58.83; H, 10.62; N, 2.86. Found: C, 59.92; H, 10.88; N, 2.99. IR. (KBr): 900 cm^{-1} $\nu_1(A_1)$ or $\nu(CrO_3)$, 948 cm^{-1} $\nu_4(E)$ or $\nu(CrO_3)$ and 431 cm^{-1} $\nu_2(A_1)$ or ν(Cr-Cl). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.9 (3H, *t*, $-CH_2-CH_3$), 1.34 (4H, *m*, $-(CH_2)_2-CH_3$), 1.42 (2H, *q*, $-CH_2-CH_2$), 1.73 (2H, *q*, $-CH_2-CH_2$), 3.3 (2H, *q*, $-CH_2-N$);^{13}C-NMR (125 MHz, DMSO-d_6) δ: 13.2, 22.4 (2C), 26.7, 31.2, 59.97.

Electronic at 455 nm, corresponding to $1a_2 \rightarrow 9e$ (ε = 200 M^{-1}cm^{-1}); 363 nm to $8e \rightarrow 9e$ (ε = 1317 M^{-1}cm^{-1}); and 283 nm to $12a_1 \rightarrow 9e$ (ε =1804 M^{-1}cm^{-1}).

Oxidation of alcohols with THACC: General Method

To a stirred solution of each alcohol (25 ml) of CH_2Cl_2, tetrahexylammonium chlorochromate (10 mmol) is added in one portion, at room temperature. The progresses of the reactions are monitored by TLC and UV/Visible spectrophotometry. The mixture were stirred and refluxed for the time indicated in the Table 1 at room temperature, diluted with CH_2Cl_2 and filtered. Evaporation of solvent furnished the product. The molar ratios of substrate to oxidants were 1:1. The solution became homogeneous briefly before the black-brown reduced reagent precipitated. Products are characterized by comparison with authentic samples (NMR, IR, TLC and mp/bp measurement).

The mixture was diluted with ether (1:1 vol/vol) and filtered through a short column of silica gel to give a clear solution. The solution was evaporated and the residual product purified by distillation, recrystallization or column chromatography. Analysis of the mixture for corresponding carbonyl compounds was accomplished by the procedure reported in earlier papers [3–6].

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