

The Two New Tripropylammonium Halochromates, $(C_3H_7)_3NH[CrO_3X]$, (X=F, Cl), Reagents for Oxidation of Alcohols on Alumina

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ABSTRACT

Two new, mild and stable chromium (VI) reagents from tripropylamine are described. Orange solids tripropylammonium fluorochromate(VI) $(C_3H_7)_3NH[CrO_3F]$, (TriPAFC), and tripropylammonium chlorochromate(VI) $(C_3H_7)_3NH[CrO_3Cl]$, (TriPACC), absorbed on alumina are easily prepared in nearly quantitative yield by the interaction of tripropylamine with CrO_3 and the corresponding acid. These reagents are versatile reagents for the effective and selective oxidation of organic substrates, in particular for alcohols, under mild conditions.

Keywords: Tripropylammonium Fluorochromate(VI); Tripropylammonium Chlorochromate (VI); Heterogeneous Oxidants; Alumina; Oxidation.

INTRODUCTION

Oxidation of organic compounds in general, and of alcohols in particular, under mild, aprotic conditions is an important reaction in synthetic organic chemistry [1]. For this purpose different Cr(VI) based oxidants are reported in the literature. However, some of the reported chromium reagents suffer from disadvantages such as instability, hygroscopicity, low selectivity, long reaction time, difficulty of preparation and need for a large excess of the reagent. Thus a milder, more selective and inexpensive reagents are much more useful. Extensive work has led to the development of a good number of these oxidants such as the Collins reagent, chromium trioxide-3,5-dimethylpyrazole complex, pyridinium chlorochromate(PCC), cetyltrimethylammonium Bromochromate, 2,2'-bipyridinium chlorochromate (BIPCC), 4-Benzylpyridinium Fluorochromate, quinolinium chlorochromate, 3,5-dimethylpyrazolium fluorochromate and tetramethylammonium fluorochromate(VI) (TMAFC) [2-10]. We now here introduce tripropylammonium fluorochromate(VI), (TriPAFC), and tripropylammonium chlorochromate(VI)

(TriPACC) absorbed on alumina as new promising reagents with improved work-up efficiency and durability, for the oxidation of alcohols.

MATERIALS AND METHODS

CrO₃ (Merck, P.A.) was used as received without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. Proton, ¹³C, ¹⁹F NMR (for TriPAFC) were carried out on a Bruker AVANCE DRX 500 spectrometer at 500, 125, 470.66 MHz. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ¹H and ¹³C NMR spectra were referenced to external SiMe₄ and ¹⁹F NMR spectra to external CFCl₃. Chromium was estimated iodometrically. In the case of the reduced product of the reagent, chromium was determined after reoxidation with acidic peroxodisulfate (K₂S₂O₈) solution. The relative concentrations of carbon, hydrogen and nitrogen were obtained from the Microanalytical laboratories, Department of Chemistry, OIRC, Tehran. Melting points were measured on Electrothermal 9100 melting point apparatus.

Synthesis of Tripropylammonium Fluorochromate, (C₃H₇)₃NH[CrO₃F](TriPAFC)

A 1g (10 mmol) sample of chromium (VI) oxide, CrO₃, and 0.9 ml (20 mmol) of 40% hydrofluoric acid were added to 20 ml of water in a 100 ml polyethylene beaker with stirring. After 5-7 min the homogeneous solution was cooled to ca. 3-5 °C. To the resultant clear orange solution, tripropylamine (1.4 ml, 10 mmol) was added dropwise with stirring over a period of 0.5 h and stirring was continued for 0.5 h at -4 °C. The precipitated yellowish-orange solid was isolated by filtration on a polyethylene funnel, washed with petroleum ether (3 × 60 ml) and dried in vacuum for 2 h at room temperature. Yield: (98%); mp 142 °C, C₉H₂₂CrFNO₃: Calc. C, 41.04; H, 8.42; N, 5.31 Found: C, 41.22; H, 8.46; N, 5.02. I.R. (KBr): 904 cm⁻¹ ν₁(A₁) or ν(CrO₃), 647 cm⁻¹ ν₂(A₁) or ν(Cr-F), 949 cm⁻¹ ν₄(E) or ν(CrO₃), Electronic absorption at 22321 cm⁻¹, corresponded to ¹A₂→¹E (ε = 140 M⁻¹cm⁻¹); 28725 m⁻¹ to ¹E→¹E (ε = 667 M⁻¹cm⁻¹) and 35971 cm⁻¹ to ¹A₁→¹E (ε = 1287 M⁻¹cm⁻¹). UV/Visible, ¹³C NMR, ¹H NMR and ¹⁹F NMR were all consistent with the TriPAFC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution of TriPAFC in water was 3.3.

Synthesis of Tripropylammonium Chlorochromate, (C₃H₇)₃NH[CrO₃Cl] (TriPACC)

Chromium (VI) oxide (1.0 g, 10 mmol) was dissolved in water in a beaker and hydrochloric acid (0.251 ml, 15 mmol) was added with stirring at 0 °C. To the resultant clear orange solution, tripropylamine (1.4 ml, 10 mmol) was added dropwise with stirring over a period of 0.5 h and stirring was continued for 0.5 h at -4 °C. The precipitated orange solid was isolated by filtration, washed with anhydrous ether (3 × 60 ml) and dried in vacuum for 2 h at room temperature. Yield: (95%); mp 135 °C. C₉H₂₂ClCrNO₃: Calc. C, 38.64; H, 7.871; N, 5.008 Found: C, 37.93; H, 7.75; N, 4.88. I.R. (KBr): 901 cm⁻¹ ν₁(A₁) or ν(CrO₃), 432 cm⁻¹ ν₂(A₁) or ν(Cr-Cl), 949 cm⁻¹ ν₄(E) or ν(CrO₃). Electronic absorption at 22123 cm⁻¹, corresponded to ¹A₂→¹E (ε = 351 M⁻¹cm⁻¹); 28169 m⁻¹ to ¹E→¹E (ε = 793 M⁻¹cm⁻¹); 35087 cm⁻¹ to ¹A₂→¹A₁ (ε = 1031 M⁻¹cm⁻¹) and 41493 cm⁻¹ to ¹A₁→¹E (ε = 219 M⁻¹cm⁻¹). UV/Visible, ¹³C NMR and ¹H NMR were all consistent with the TriPACC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution TriPACC in water was 2.9.

The general procedure for supporting of TriPAFC and TriPACC on alumina

For supporting of the TriPAFC and TriPACC on alumina, in synthetic procedures alumina (mesh 65-250) was added before the tripropylamine addition step. The supported reagents were separated and washed by cold water and acetone. The oxidizing capacity of the supported

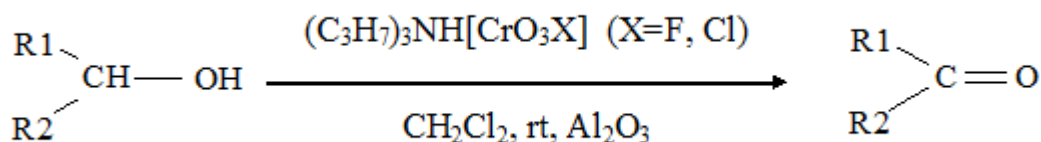
reagents was determined by stirring overnight 0.5 g of the supported reagents with 10 ml of 2N aqueous potassium hydroxide, filtering off and titrating iodometrically the obtained chromate solution. The determined average capacity of the dried supported for the above reagents are 1-1.5 mmol of TriPAFC per 1 g of silica gel and 1.3- 1.6 mmol of TriPACC per 1 g of alumina. The supported reagents so obtained did not noticeably lose their activities neither on storing in air at room temperature for several weeks nor on refluxing for 5 h in benzene or hexane.

General procedure for oxidation of organic substrates with TriPAFC and TriPACC on alumina

To a stirred suspension of tripropylammonium halochromate absorbed on alumina in dichloromethane (generally 5 ml), a solution of the substrate in the minimum amount of dichloromethane was added dropwise (Table 1). Completion of the reaction was followed by TLC with using ether/petroleum ether (60/40) as eluant. The mixture was diluted with ether (1:1 v/v) and filtered through a short column of alumina to give a clear solution. The solution was evaporated and the residual product purified by distillation, recrystallization or column chromatography.

RESULTS AND DISCUSSION

Our supported reagents are remarkably effective in oxidizing primary and secondary alcohols to aldehydes and ketones in high yields. Different primary and secondary alcohols were subjected to oxidations with tripropylammonium fluorochromate(VI), (TriPAFC), and tripropylammonium chlorochromate(VI), (TriPACC), are absorbed on Al_2O_3 in dichloromethane (Schem1). These oxidations take place under mild and completely heterogeneous conditions giving excellent yields (Table 1).



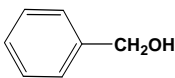
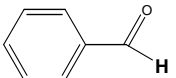
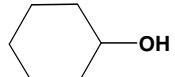
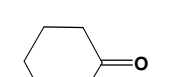
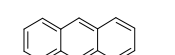
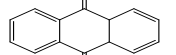
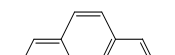
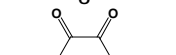
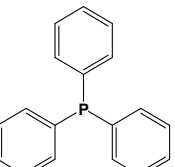
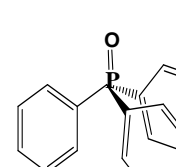
The heterogeneous reaction mixtures are thoroughly stirred, at room temperature. The corresponding aldehyde and ketone products can then be easily isolated by simple filtration and evaporation of the solvent

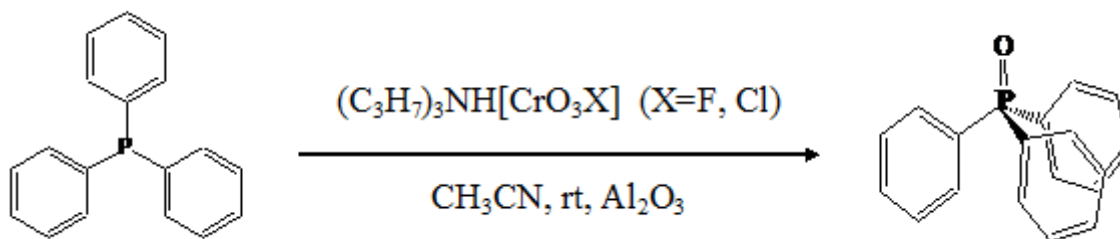
Oxidations may also occur using TriPAFC and TriPACC, in the absence of Al_2O_3 , but considerable yield improvements are observed in the presence of the absorbent. This implies that the Al_2O_3 may provide an effective heterogeneous surface area for oxidation and at the same time makes work-up much more convenient [9].

The nature of the solvent does not appear to be particularly critical. Hydrocarbons, benzene, ethers and chlorinated hydrocarbons are equally effective; the practical choices were being oriented by the solubility of the products and the desired reaction temperature. The chromium (VI) contents in the products determined iodometrically [10].

The reaction of triphenylphosphine with TriPAXC (X=F, Cl) (molar ratio of PPh_3 : TriPAXC = 1:1.1) in acetonitrile were carried out at room temperature and triphenylphosphine oxide was obtained in a quantitative yield. These provide clear-cut examples of oxygen transfer reactions involving TriPAFC and TriPACC, and the result may also be useful in defining other related reactions (Scheme 2).

Table 1: Oxidations of Organic Substrates via TriPAFC and TriPACC on Alumina

	Substrate	Product	TriPAFC		TriPACC	
			Time (min)	Yield (%)	Time (min)	Yield (%)
1	$n\text{-C}_6\text{H}_{13}\text{-OH}$	$n\text{-C}_5\text{H}_{11}\text{-CHO}$	162	90	335	92
2	$n\text{-C}_8\text{H}_{17}\text{-OH}$	$n\text{-C}_7\text{H}_{15}\text{-CHO}$	200	90	230	97
3	$3\text{-C}_7\text{H}_{15}\text{-OH}$	$3\text{-C}_7\text{H}_{14}\text{O}$	220	90	280	92
4	$2\text{-C}_8\text{H}_{17}\text{-OH}$	$2\text{-C}_8\text{H}_{16}\text{O}$	225	90	270	90
5	$2\text{-C}_{11}\text{H}_{23}\text{-OH}$	$2\text{-C}_{11}\text{H}_{22}\text{O}$	108	90	168	95
6			85	90	95	91
7			11h	90	370	93
8			6h	67	350	90
9			6h	64	350	97
10			20	90	26	88
			15	90	20	86



The IR spectra of TriPAFC and TriPACC are similar to that of other fluoro and chlorochromates [11]. TriPAFC and TriPACC are soluble in water, dimethylformamide, acetonitrile, acetone and dichloromethane. They are only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane. During the reactions, the color of the oxidant changes from orange to brown, providing visual means for ascertaining the progress of the oxidation. The results obtained with

TriPAXC (X=F, Cl) on alumina are very satisfactory and shows the new reagents as a valuable addition to the existing oxidizing agents.

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