December 2006 Volume 2 Issue 5-6

Trade Science Inc.

Organic CHEMISTRY

An Indian Journal

Full Paper

OCAIJ, 2(5-6), 2006 [170-173]

Synthesis And Reactions Of Tripropylammonium Halochromates(VI), $(C_3H_7)_3NH[Cro_3x]$, (X=F, Cl) On Silica Gel, Selective And Efficient Heterogeneous Oxidants

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Received: 31st October, 2006
Accepted: 15th November, 2006

Web Publication Date : 28th December, 2006

ABSTRACT

Tripropylammonium fluorochromate(TriPAFC) and tripropylammonium chlorochromate(TriPACC) are new efficient reagents, which are prepared easily and oxidize primary and secondary alcohols to the corresponding aldehydes or ketones. The durability, ease of work up and efficiency of (TriPAHC) are considerably increased upon its absorption on silica gel.

KEYWORDS

Tripropylammonium fluorochromate(VI);
Tripropylammonium chlorochromate (VI);
Heterogeneous;
Oxidants;
Silica gel;
Oxidation alcohols.

INTRODUCTION

The search for new oxidizing agents is of interest to synthetic organic chemists. Many such reagents have been developed in recent years with some success. In particular, there is 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. In recent years, significant improvements were achieved by the use of new oxidizing agents[1-3], such as 3-carboxypyridinium chlorochromate[4], pyridinium fluorochromate[5]. Quinolinium dichromate[6], caffeinilium chlorochromate[7], quinolinium chloro-chromate[8], isoquinolinium fluorochromate[9] and tetramethylammonium fluorochromate[10]. We have now investigated the synthetic potential of tripropylammonium fluorochromate, $C_9H_{22}CrFNO_3$, (TriPAFC) and tripropylammonium chlorochromate, $C_9H_{22}ClCrNO_3$, (TriPACC), and we have found that these reagents have certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, easier working up and high yields. Further, tripropylammonium halochromates do not react with acetonitrile, which is a suitable medium for studying kinetics and mechanism.

This manuscript introduces tripropylammonium fluorochromate(VI) (TriPAFC) and tripropylammonium chlorochromate(VI) (TriPACC) absorbed on silica gel as new promising reagents with improved work-up efficiency and durability, for the oxidation of alcohols to their corresponding aldehydes and ketones, under mild conditions.

EXPERIMENTAL

CrO_3 (P.A.Merck) was used 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, ^{13}C, ^{19}F NMR(for TriPAFC) were carried out on a Bruker AVANCE DRX 500 spectrometer at 500, 125, 470.66MHz. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ^1H and $^{13}CNMR$ spectra were referenced to external $SiMe_4$ and $^{19}FNMR$ spectra to external $CFCl_3$. Chromium was estimated iodometrically. In the case of the reduced product of the oxidant, chromium was determined after oxidizing with acidic peroxodisulfate($K_2S_2O_8$) 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. A microsynth. milstone laboratory microwave oven has been used.

Synthesis of tripropylammonium chlorochromate, (TriPACC), $(C_3H_7)_3NH\ [CrO_3Cl]$

Chromium(VI) oxide(1.0g, 10mmol) was dissolved in water in a beaker and hydrochloric acid (0.251ml, 15mmol) was added with stirring at 0°C. To the resultant clear orange solution, tripropylamine (1.4ml, 10mmol) was added dropwise with stirring to this solution over a period of 0.5h and stirring was continued for 0.5h at -4°C. The precipitated orange solid was isolated by filtration, washed with anhydrous ether(3×60ml) and dried in vacuum for 2h at room temperature. Yield:(95%); mp 135°C. $C_9H_{22}ClCrNO_3$:Calc. C, 38.64; H, 7.871; N, 5.008 Found: C, 37.93; H, 7.75; N, 4.88. IR(KBr): 901 cm^{-1} $\nu_1(A_1)$ or ν (CrO_3), 432 cm^{-1} $\nu_2(A_1)$ or ν (Cr-Cl), 949 cm^{-1} $\nu_4(E)$ or $\nu(CrO_3)$. Electronic absorption at 22123 cm^{-1}, corresponded to $^1A_2 \rightarrow {}^1E$ (ε = 351 $M^{-1}cm^{-1}$); 28169 m^{-1} to $^1E \rightarrow {}^1E$(ε = 793 $M^{-1}cm^{-1}$); 35087 cm^{-1} to $^1A_2 \rightarrow {}^1E$(ε = 1031 $M^{-1}cm^{-1}$) and 41493 cm^{-1} to $^1A_2 \rightarrow {}^1E$(ε = 219 $M^{-1}cm^{-1}$). UV/Visible, $^{13}CNMR$ and ^1HNMR were all consistent with the TriPACC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01M solution TriPACC in water was 2.9

Synthesis of tripropylammonium fluorochromate (TriPAFC), $(C_3H_7)_3NH[CrO_3F]$

A 1g (10mmol) sample of chromium(VI) oxide, CrO_3, and 0.9ml(20mmol) of 40% hydrofluoric acid were added to 20ml of water in a 100ml polyethylene beaker with stirring. After 5-7min. The homogeneous solution was cooled to ca. 0-2°C. To the resultant clear orange solution, tripropylamine(1.4ml, 10mmol) was added dropwise with stirring over a period of 0.5h and stirring was continued for 0.5h 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, $C_9H_{22}CrFNO_3$:Calc. C, 41.05; H, 8.35; N, 5.31 Found: C, 41.22; H, 8.46; N, 5.02. IR(KBr): 904 cm^{-1} $\nu_1(A_1)$ or ν (CrO_3), 647 cm^{-1} $\nu_2(A_1)$ or ν (Cr-F), 949cm^{-1} $\nu_4(E)$ or ν (CrO_3), electronic absorption at 22321cm^{-1}, corresponded to $^1A_2 \rightarrow {}^1E$(ε= 140 $M^{-1}cm^{-1}$); 28729cm^{-1} to $^1E \rightarrow {}^1E$(ε=667$M^{-1}cm^{-1}$) and 35951cm^{-1} to $^1A_2 \rightarrow {}^1E$ (ε=1287 $M^{-1}cm^{-1}$). UV/Visible, $^{13}CNMR$, ^1HNMR and $^{19}FNMR$ were all consistent with the TriPAFC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01M solution of TriPAFC in water was 3.3.

General procedure for oxidation of organic substrates with TriPAFC and TriPACC

To a stirred suspension of tripropylammonium halochromate absorbed on silica gel in dichloromethane (generally 5cm^3), a solution of the substrate in the minimum amount of dichloromethane were added drop wise (TABLE 1). The completion of the reaction was followed by TLC using ether/petroleum ether(60/40) as eluant. The mixture is diluted with ether(1:1v/v) 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.

Reaction of TriPAFC with triphenylphosphine

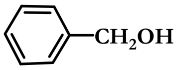
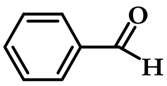
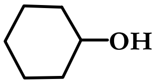
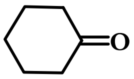
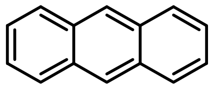
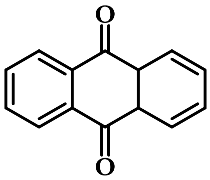
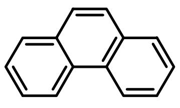
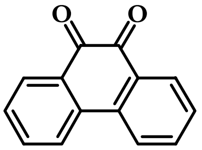
The reaction was performed under nitrogen atmosphere in a dry 100mL round bottomed flask and under efficient stirring. To a vigorously stirred solution of 1.50g(5.72 mmol) of triphenylphosphine in 35mL of acetonitrile, 1.65g(6.29mmol) of Tri-PAFC was added in two installments in about one minute, maintaining the substrate: oxidant ratio at 1:1.1. An exothermic reaction set in instantaneously, and was complete in 5min. The solution was cooled and the mother liquor and the washings, after separation of reduced TriPAFC product by centrifugation, were filtered through a short silica gel column(7.2cm^2). The contents of the column were thoroughly washed with ether(3.35mL) and filtered. The combined filtrates were evaporated on a steam bath, and the product was characterized as triphenyl-phosphine oxide by elemental analyses and IR spectral studies. Yield: 1.56g(98%). mp:Found, 155°C(Lit.mp. 156-157°C)

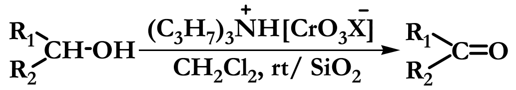
RESULTS AND DISCUSSION

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) absorbed on SiO$_2$ in dichloromethane (SCHEME 1). 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 al-

TABLE 1: Oxidations via TriPACC and TriPAFC on silica gel

	Substrate	Product	TriPAFC		TriPACC	
			Time (min)	Yield (%)	Time (min)	Yield(%)
1	n-C_6H_{13}-OH	n-C_5H_{11}-CHO	160	90	305	94
2	n-C_8H_{17}-OH	n-C_7H_{15}-CHO	195	90	220	90
3	3-C_7H_{15}-OH	3-C_7H_{14}O	220	90	255	95
4	2-C_8H_{17}-OH	2-C_8H_{16}O	215	90	250	94
5	2-$C_{11}H_{23}$-OH	2-$C_{11}H_{22}$O	105	90	150	93
6			85	92	75	91
7			10	85	370	89
8			6h	67	350	91
9			6h	67	350	88



(1) (2)

SCHEME 1

dehyde and ketone products can then be easily isolated by simple filtration and evaporation of the solvent

Oxidations may also occur using only TriPAFC and TriPACC, in the absence of SiO_2, but considerable improvements are observed in the presence of the absorbent. This implies that the SiO_2 may act as a reaction medium, providing an effective heterogeneous surface area for the oxidation and at the same time making the work-up much more convenient[11].

The nature of the solvent does not appear to be particularly critical. Hydrocarbons, benzene, ethers and chlorinated hydrocarbons are equally effective, the practical choice being oriented by the solubility of the products and the desired reaction temperature. The chromium(VI) contents easily determined iodometrically[12].

The IR spectra of TriPAFC and TriPACC are similar to that of other fluoro and chlorochromates[13], TriPAFC and TriPACC are soluble in water, dimethylformamide, acetonitrile, acetone and dichloromethane; they are only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane

ACKNOWLEDGMENTS

The author thanks Dr.A.R.Mahjoub and Mrs.S.Khorsandtabar and Mr.S.Bagi for valuable discussion

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