Oxidation of Organic Substrates Using Two Triethylammonium Halochromates(VI), $(C_2H_5)_3NH[CrO_3X]$, (X=F, CI) Supported on Silica Gel

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Triethylammonium fluorochromate(VI), $(C_2H_5)_3$ NHCrO₃F, TriEAFC and triethylammonium chlorochromate(VI), $(C_2H_5)_3$ NHCrO₃Cl, TriEACC were prepared, supported on silica gel and used to quantitatively oxidize a number of organic substrates. These supported triethylammonium halochromates are versatile reagents ensuring effective oxidation of organic compounds, in particular of alcohols, under mild conditions. The durability, ease of work up and efficiency of TriEAFC and TriEACC are considerably increased upon their absorption on silica gel.

Keywords: Triethylammonium fluorochromate(VI); Triethylammonium chlorochromate(VI); Heterogeneous oxidants; Silica gel; Oxidation; Alcohols.

Scheme I

INTRODUCTION

The development of oxidizing agents based upon higher-valent transition metal oxo derivatives has been a subject of research in many laboratories, and a host of such reagents derived from ruthenium, osmium, iron, manganese, molybdenum, vanadium and chromium have all proven to be capable of alcohol oxidation. 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 pyridinum fluorochromate,⁵ quinolinium dichromate,⁸ isoquinolinium fluorochromate,⁹ and tetramethylammonium fluorochromate.¹⁰

This manuscript introduces triethylammonium fluorochromate(VI) (TriEAFC) and triethylammonium chlorochromate(VI) (TriEACC) 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.

RESULTS AND DISCUSSION

The results obtained with triethylammonium fluorochromate(VI) and triethylammonium chlorochromate(VI) absorbed on silica gel, are very satisfactory and show the new reagents to be valuable additions to the existing oxidizing agents. Table 1 summarizes the products, yields and reaction times of TriEAFC and TriEACC absorbed on silica gel, with various substrates.



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 only TriEAFC and TriEACC, in the absence of SiO₂, but considerable improvements are observed in the presence of the absorbent. This implies that the SiO₂ 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) con-

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Substrate		Product	TriEAFC		TriEACC	
			Time	Yield	Time	Yield
			(min)	(%)	(min)	(%)
1	<i>n</i> -C ₆ H ₁₃ -OH	<i>n</i> -C ₅ H ₁₁ -CHO	180	90	345	95
2	<i>n</i> -C ₈ H ₁₇ -OH	<i>n</i> -C ₇ H ₁₅ -CHO	218	90	250	69
3	3-С ₇ Н ₁₅ -ОН	$3-C_7H_{14}O$	245	90	300	94
4	2-С ₈ Н ₁₇ -ОН	$2 - C_8 H_{16} O$	240	90	275	95
5	2-С ₁₁ Н ₂₃ -ОН	$2 - C_{11}H_{22}O$	124	90	240	97
6	СН2ОН	⟨	92	92	95	99
7	ОН	— •	12h	90	380	91
8			6h	65	480	95
9			6h	63	480	96

Table 1. Oxidations via TriEACC and TriEAFC on silica gel

tents are easily determined iodometrically.¹²

Triethylammonium halochromates are easily prepared in high yields from chromium(VI) oxide, triethylamine and aqueous related acid (HCl or HF) in a convenient molar ratio. The bright orange crystalline reagents can be stored in polyethylene containers for long periods without decomposition. The IR spectra of the reagents are similar to that of other halochromates. Triethylammonium halochromates are soluble in water, dimethylformamide¹³ acetonitrile and acetone; they are less soluble in dichloromethane and only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

EXPERIMENTAL

Material and Instruments

CrO₃ (Merck, P. A.) 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, ¹³C, and ¹⁹F NMR (for TriEAFC) 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 ox-

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 an Electrothermal 9100 melting point apparatus.

Triethylammonium Fluorochromate (TriEAFC), (C₂H₅)₃NH[CrO₃F]

A 1 g (10 mmol) sample of chromium(VI) oxide, CrO₃, and (0.9 mL, 20 mmol) of 40% hydrofluoric acid was added to 20 mL of water in a 100 mL polyethylene beaker with stirring. After 5 min the homogeneous solution was cooled to approx. 0-2 °C. To the resultant clear orange solution, triethylamine (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 $(3 \times 60 \text{ mL})$ and dried in vacuum for 2 h at room temperature. Yield: (88%); mp 132 °C, C₆H₁₆CrFNO₃: Calc. C, 32.57; H, 7.23; N, 6.33. Found: C, 32.08; H, 7.64; N, 6.44. I.R. (KBr): 904 $cm^{-1}v_1(A_1)$ or v(CrO₃), 648 cm⁻¹v_2(A_1) or v(Cr-F), 948 $cm^{-1}v_4(E)$ or v(CrO₃), Electronic absorption at 22321 cm⁻¹, corresponded to ${}^{1}A_{2} \rightarrow {}^{1}E$ ($\epsilon = 270 \text{ M}^{-1}\text{cm}^{-1}$); 28735 m⁻¹ to ${}^{1}E \rightarrow {}^{1}E$ ($\varepsilon = 845 \text{ M}^{-1}\text{cm}^{-1}$) and 36231 cm⁻¹ to ${}^{1}A_{2} \rightarrow {}^{1}E$ ($\varepsilon =$ 1233 $M^{-1}cm^{-1}$). ¹H-NMR (500 MHZ, CD₃CN): $\delta = 1.2$ (t, 3H, -CH₃), $\delta = 2.7$ (t, 2H, -CH₂-), $\delta = 7.5$ ppm (s, 1H, -NH), ¹³C-NMR (124.44 MHZ, CD₃CN): δ 8.10, 53.35. ¹⁹F-NMR of this oxidant shows signal at 161 ppm. UV/Visible, ¹³C NMR, ¹H NMR and ¹⁹F NMR were all consistent with the TriEAFC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution of TriEAFC in water was 3.45.

Triethylammonium Chlorochromate (TriEACC), (C₂H₅)₃NH[CrO₃Cl]

Chromium(VI) oxide (1.0 g, 10 mmol) was dissolved in water in a beaker and 6 M hydrochloric acid (0.25 cm^3 , 15 mmol) was added under stirring at 0 °C. To the resultant clear orange solution, triethylamine (0.1 cm^3 , 10 mmol) was added dropwise under stirring over a period of 0.5 h

and the stirring was continued for 0.5 h at -4 °C. The precipitated clear orange solid was isolated by filtration, washed with petroleum ether $(3 \times 60 \text{ cm}^3)$ and dried under vacuum for 2 h at room temperature. Yield: (54%); mp 120 °C. Calcd. For C₆H₁₆ClCrNO₃: C, 30.315; H, 6.736; N, 5.894. Found: C, 30.29; H, 6.81; N, 5.82. IR (KBr): 900 $cm^{-1} v_1(A_1) \text{ or } v(CrO_3), 434 cm^{-1} v_2(A_1) \text{ or } v(Cr-Cl), 950$ $cm^{-1}v_4(E)$ or $v(CrO_3) cm^{-1}$. UV/Visible and ¹H-NMR were all consistent with the TriEACC structure. Electronic absorption at 22075 cm⁻¹, corresponding to ${}^{1}A_{2} \rightarrow {}^{1}E$ ($\epsilon = 316$ dm³ mol⁻¹ cm⁻¹); 28169 cm⁻¹ to ${}^{1}E \rightarrow {}^{1}E$ ($\epsilon = 803 \text{ dm}^{3} \text{ mol}^{-1}$ cm⁻¹); 35087.7 cm⁻¹ to ${}^{1}A_{2} \rightarrow {}^{1}A_{1}$ ($\epsilon = 1065 \text{ dm}^{3} \text{ mol}^{-1} \text{ cm}^{-1}$) and 41152 cm⁻¹ to ${}^{1}A_{1} \rightarrow {}^{1}E$ ($\varepsilon = 1327 \text{ dm}^{3} \text{ mol}^{-1} \text{ cm}^{-1}$). ¹H-NMR (500 MHZ, CD₃CN): $\delta = 1.22$ (t, 3H, -CH₃), $\delta =$ 2.9 (t, 2H, -CH₂-), δ = 7.6 ppm (s, 1H, -NH), ¹³C-NMR (124.44 MHz, CD₃CN): δ 8.15, 53.45. UV/Visible, ¹³C NMR and ¹H NMR were all consistent with the TriEACC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution of TriEAFC in water was 2.4.

General procedure for supporting on silica gel

For support of the TriEAFC and TriEACC on silica gel, in the synthesizing process silica gel (mesh 65-250) was added before the triethylamine addition step. The supported reagents separated and were washed by cold water and acetone. The capacity of the supported reagents were determined by stirring overnight 0.5 g of the supported reagents with 10 mL of 2 N aqueous potassium hydroxide, filtering off and titrating iodometrically the obtained chromate solution. The determined average capacity of the dried support for the above reagents is 1.6-2 mmol of TriEAFC per 1 g of silica gel and 1.4-2.1 mmol of TriEACC per 1 g of silica gel. The supported reagents so obtained did not noticeably lose their activities either on storing in air at room temperature for several weeks or on refluxing for 5 h in benzene or hexane.

General procedure for oxidation of organic substrates with TriEAFC and TriEACC

To a stirred suspension of triethylammonium halochromate absorbed on silica gel in dichloromethane (generally 5 cm³), a solution of the substrate in the minimum amount of dichloromethane was added dropwise (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 (1:1 v/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.

HAZARDS

Always work in the fume hood. Organic solvents such as toluene, acetone, hexanes, acetonitrile, dichloromethane, ether and petroleum ether are volatile and flammable. Acidic Chromic Acid is corrosive.

DANGER! Strong oxidizer contact with other materials may cause a fire.

CORROSIVE, Causes severe burns to every area of contact.

Both it and the solid-support contain chromium, a heavy metal, and are potentially environmentally damaging so handle and dispose of it as instructed. Some of the compounds are irritants. HARMFUL IF SWALLOWED OR INHALED, Affects the respiratory system, liver, kidneys, eyes, skin and blood. May cause allergic reaction. CANCER HAZARD. CAN CAUSE CANCER. Risk of cancer depends on duration and level of exposure.

CONCLUSIONS

The new reagents triethylammonium chlorochromate(VI), (TriEACC) and triethylammonium fluorochromate(VI), (TriEAFC) absorbed on silica gel, are easily synthesized. They prove to be low cost and readily available oxidizing reagents for a variety of alcohols. Their advantages include higher yields, shorter reaction times, lower alcohol/oxidant molar ratios, application to pH sensitive molecules and ease of separation of products (Table 1). Moreover, during the reaction, the color of the oxidants changes from orange to brown, thus providing a visual means for ascertaining the progress of the oxidation. Many functional groups are inert towards these oxidizing agents enhancing the usefulness of the oxidant and the oxidation conditions for the synthesis of highly functionalized molecules.⁷⁻¹⁰

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