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Oxidation of Diols Using Trialkylammonium fluorochromates(VI), $R_3NH[CrO_3F]$, ($R= CH_3$, C_2H_5, C_3H_7 and C_4H_9) Supported on Silica Gel and Alumina

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Abstract

A number of new chromium(VI) supported reagents Trialkylammonium fluorochromates(VI), $R_3NH[CrO_3F]$, ($R= CH_3$, C_2H_5, C_3H_7 and C_4H_9) (TriRAFC) has been developed by reacting trialkylamine with CrO_3 and aqueous HF. These reagents are versatile reagents for the effective and selective oxidation of organic substrates, in particular for diols, under mild and heterogeneous conditions on silica gel and alumina.

Keywords: Trialkylammonium fluorochromates(VI); oxidation; diols; heterogeneous oxidants; silica gel; alumina

Introduction

The oxidation of organic substrates in aprotic solvents, under mild and neutral conditions, is important in modern organic synthesis. Therefore, 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[1]. In particular; there is continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of organic substrates, under mild conditions. Of the large number of "mild" chromium based oxidizing agents available, many prove impractical when the reactions are performed on a large (mol) scale,[2] although in recent years, significant improvements have been achieved by the use of new oxidizing agents.[3-5] Examples are: pyridinium chlorochromate,[6] pyridinium dichromate,[7] pyridinium fluorochromate[8], 2, 2'–bipyridinium chlorochromate[9], tripropylammonium fluorochromate[10] and tetramethylammonium fluorochromate (TMAFC)[11]. *In continuation of our ongoing work on development of highly efficient oxidation process, we observed that the oxidation of diols with solid state supported Trialkylammonium fluorochromates*(VI) $R_3NH[CrO_3F]$, ($R= CH_3$, C_2H_5, C_3H_7 and C_4H_9) (TriRAFC) at room temperature could be carried out much more convenient.

Results and Discussion

Our supported reagents are remarkably effective in oxidation diols in high yields. Diols were subjected to oxidations with Trialkylammonium fluorochromates(VI), $R_3NH[CrO_3F]$, ($R= CH_3$, C_2H_5, C_3H_7 and C_4H_9) (TriRAFC) absorbed on SiO_2 and Al_2O_3. These oxidations take place under mild and completely heterogeneous conditions giving excellent yields (Scheme 1)(Table 1 and 2).

$$HO\text{-}CH_2\text{-}(CH_2)_n\text{-}CH_2OH \xrightarrow[CH_2Cl_2\ ,\ rt/\ SiO_2/Al_2O_3]{R_3\overset{+}{N}H[CrO_3\overset{-}{F}]} HO\text{-}CH_2\text{-}(CH_2)_n\text{-}CHO$$

(Sheme 1)

Table 1. Oxidation via TriRAFC Supported on Silica gel

Substrate	Product	R= CH_3		R= C_2H_5		R= C_3H_7		R= C_4H_9	
		Time	Yield	Time	Yield	Time	Yield	Time	Yield

			(min)	(%)	(min)	(%)	(min)	(%)	(min)	(%)
1	$HO-CH_2-CH_2-OH$	$HO-CH_2-CHO$	315	90	325	87	320	91	330	89
2	$HO-CH_2-CH-CH_3$	$CH_3-CH-CHO$	300	90	310	89	298	92	315	86
3	$HO-(CH_2)_4-OH$	$HO-(CH_2)_3-CHO$	282	90	280	89	279	92	298	88
4	$CH_3-CH(OH)-CH(OH)-CH_3$	$CH_3-CH(OH)-CO-CH_3$	290	90	287	89	285	91	287	87

Table 2. Oxidation via TriRAFC Supported on Alumina

Substrate		**Product**	**R= CH_3**		**R= C_2H_5**		**R= C_3H_7**		**R= C_4H_9**	
			Time (min)	**Yield (%)**	**Time (min)**	**Yield (%)**	**Time (min)**	**Yield (%)**	**Time (min)**	**Yield (%)**
1	$HO-CH_2-CH_2-OH$	$HO-CH_2-CHO$	320	90	324	89	318	93	330	85
2	$HO-CH_2-CH-CH_3$	$CH_3-CH-CHO$	300	89	305	87	295	95	312	88
3	$HO-(CH_2)_4-OH$	$HO-(CH_2)_3-CHO$	285	91	287	88	284	92	295	89
4	$CH_3-CH(OH)-CH(OH)-CH_3$	$CH_3-CH(OH)-CO-CH_3$	292	88	290	89	285	90	292	87

The heterogeneous reaction mixtures are thoroughly stirred, at room temperature. Oxidations may also occur using only TriRAFC, in the absence of SiO_2 and Al_2O_3 but considerable improvements are observed in the presence of the absorbent. This implies that the SiO_2 and Al_2O_3 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.

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.

The IR spectra of TriRAFC are similar to that of other fluorochromates[12]. TriRAFC is soluble in water, dimethylformamide, acetonitrile, acetone and dichloromethane; they are only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

Experimental Section

CrO_3 (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, ^{13}C, ^{19}F NMR 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; ^{1}H and ^{13}C NMR spectra were referenced to external $SiMe_4$ and ^{19}F NMR 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.

Trimethylammonium Fluorochromate (TriMAFC), $(CH_3)_3NH[CrO_3F]$

A 1g (10 mmol) sample of chromium (VI) oxide, CrO_3, and 0.9ml (20 mmol) of 40% hydrofluoric acid were added to 20 ml of water in a 100 ml polyethylene beaker with stirring. After 7 min the homogeneous solution was cooled to ca.-2 ° C. To the resultant orange solution, trimethylamine (0.01mol) with hydrofluoric aside was added drop wise with stirring over a period of 0.5 h and stirring was continued for 0.5 h at 2 °C. The precipitated clear-orange liquid 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: (86%); mp 126 °C, $C_{12}H_{28}CrFNO_3$: Calc. C, 20.11; H, 5.58; N, 7.82 Found: C, 20.08; H, 5.64; N, 7.69. I.R. (KBr): 912 cm^{-1} $\nu_1(A_1)$ or $v(CrO_3)$, 636 cm^{-1} $\nu_2(A_1)$ or ν(Cr-F), 950 cm^{-1} $\nu_4(E)$ or $\nu(CrO_3)$, Electronic absorption at 22026 cm^{-1}, corresponded to $^1A_2 \longrightarrow {}^1E$ (ε = 174 $M^{-1}cm^{-1}$); 28735 m^{-1} to $^1E \longrightarrow {}^1E$ (ε = 664 $M^{-1}cm^{-1}$) and 36231 cm^{-1} to $^1A_2 \longrightarrow {}^1E$($\varepsilon$ = 1248 $M^{-1}cm^{-1}$). UV/Visible, ^{13}C NMR, ^1H NMR and ^{19}F NMR were all consistent with the TriMAFC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution of TriMAFC in water was 2.9.

Triethylammonium Fluorochromate (TriEAFC), $(C_2H_5)_3NH[CrO_3F]$

A 1g (10 mmol) sample of chromium (VI) oxide, CrO_3, 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 min the homogeneous solution was cooled to ca. 0-2 ° C. To the resultant clear orange solution, triethylamine (1.400 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: (88%); mp 132 °C, $C_6H_{16}CrFNO_3$: 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} $\nu_1(A_1)$ or $v(CrO_3)$, 648 cm^{-1} $\nu_2(A_1)$ or ν(Cr-F), 948 cm^{-1} $\nu_4(E)$ or $\nu(CrO_3)$, Electronic absorption at 22321 cm^{-1}, corresponded to $^1A_2 \longrightarrow {}^1E$ (ε = 270 $M^{-1}cm^{-1}$); 28735 m^{-1} to $^1E \longrightarrow {}^1E$ (ε = 845 $M^{-1}cm^{-1}$) and 36231 cm^{-1} to $^1A_2 \longrightarrow {}^1E$($\varepsilon$ = 1233 $M^{-1}cm^{-1}$). UV/Visible, ^{13}C NMR, ^1H NMR and ^{19}F 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.

Tripropylammonium Fluorochromate (TriPAFC), $(C_3H_7)_3NH[CrO_3F]$

A 1g (10 mmol) sample of chromium (VI) oxide, CrO_3, 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 (1.4ml, 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, $C_9H_{22}CrFNO_3$: Calc. C, 41.05; H, 8.35; N, 5.31 Found: C, 41.22; H, 8.46; N, 5.02. I.R. (KBr): 904 cm^{-1} $\nu_1(A_1)$ or $\nu(CrO_3)$, 647 cm^{-1} $\nu_2(A_1)$ or ν(Cr-F), 949 cm^{-1} $\nu_4(E)$ or $\nu(CrO_3)$, Electronic absorption at 22321 cm^{-1}, corresponded to $^1A_2 \longrightarrow {}^1E$ (ε = 140 $M^{-1}cm^{-1}$); 28725 m^{-1} to $^1E \longrightarrow {}^1E$ (ε = 667 $M^{-1}cm^{-1}$) and 35971 cm^{-1} to $^1A_1 \longrightarrow {}^1E$($\varepsilon$ = 1287 $M^{-1}cm^{-1}$). UV/Visible, ^{13}C NMR, ^1H NMR and ^{19}F 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.

Tributylammonium Fluorochromate (TriBAFC), $(C_4H_9)_3NH[CrO_3F]$

A 1g (10 mmol) sample of chromium (VI) oxide, CrO_3, and 0.9ml (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. 0-2 ° C. To the resultant clear orange solution, tributylamine (2.35ml, 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: (84%); mp 134 °C, $C_{12}H_{28}CrFNO_3$: Calc. C, 47.20; H, 9.24; N, 4.58 Found: C, 46.92; H, 9.64; N, 5.20. I.R. (KBr): 914 cm^{-1} $\nu_1(A_1)$ or $\nu(CrO_3)$, 634 cm^{-1} $\nu_2(A_1)$ or ν(Cr-F), 950 cm^{-1} $\nu_4(E)$ or $\nu(CrO_3)$, Electronic absorption at 22321 cm^{-1}, corresponded to $^1A_2 \longrightarrow {}^1E$ (ε = 177 $M^{-1}cm^{-1}$); 28735 m^{-1} to $^1E \longrightarrow {}^1E$ (ε = 701 $M^{-1}cm^{-1}$) and 35971 cm^{-1} to $^1A_1 \longrightarrow {}^1E$($\varepsilon$ = 1314 $M^{-1}cm^{-1}$).

UV/Visible, ^{13}C NMR, ^{1}H NMR and ^{19}F NMR were all consistent with the TriBAFC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution of TriBAFC in water was 3.15.

General procedure for supporting of TriRAFC

For supporting of the TriRAFC on silica gel or alumina, in synthesizing process silica gel or alumina (mesh 65-250) were added before the trialkylamine addition step. The supported reagents separated and 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 supported for the above reagents are 1-1.8 mmol of TriRAFC per 1 g of silica gel or 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 Diols with absorbed TriRAFC

To a stirred suspension of trialkylammonium fluorochromate absorbed on silica gel or alumina in dichloromethane (generally 5 cm^3), a solution of the substrate in the minimum amount of dichloromethane were added dropwise. 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 alumina to give a clear solution. The solution was evaporated and the residual product purified by distillation, recrystallization or column chromatography. The separated compounds characterized and it is found the product in that only one of the hydroxyl groups oxidized is main product. The progress of the reactions was also monitored and checked by UV/Visible spectrophotometry. The amount of the oxidant during the reaction was measured spectrophotometrically at 363 nm. A very small magnetic stirrer was designed at the cell (10 mm quartz cell) compartment just in the bottom of sample cell in the spectrophotometer to stir up the solution under study in cell. The reaction mixtures remained homogenous in the solvent system used.

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