

Oxidation of Some Organic Diols with Trialkylammonium Fluorochromates(VI), $R_3NH[CrO_3F]$, ($R = CH_3, C_2H_5, C_3H_7$ and C_4H_9) at Room Temperature and Under Microwave Condition

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Abstract. A mild and efficient method for the mono-oxidation of diols to the corresponding hydroxyaldehydes with trialkylammonium fluorochromates(VI), $R_3NH[CrO_3F]$ ($R = CH_3, C_2H_5, C_3H_7$ and C_4H_9), in solution at room temperature, and in solution under microwave radiation, is reported. The easy procedure, simple work-up, short reaction times, and excellent yields are advantages of these reagents.

Keywords: Trialkylammonium fluorochromates(VI); oxidants; oxidation; diols; microwave; room temperature.

Resumen. Se describe un método eficiente y suave para la mono-oxidación de dioles a los hidroxialdehidos correspondientes con fluorocromatos(VI) de trialquilamonio, $R_3NH[CrO_3F]$ ($R = CH_3, C_2H_5, C_3H_7$ y C_4H_9), en solución a temperatura ambiente y en solución bajo irradiación de microondas. La facilidad del procedimiento y la sencillez de la extracción del producto, así como de los tiempos de reacción cortos y los rendimientos elevados, son una muestra de las ventajas de estos reactivos.

Palabras clave: Fluorocromatos(VI) de trialquilamonio; oxidantes; oxidación; dioles; microondas; temperatura ambiente.

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 using new oxidizing agents [3-11]. Examples are: pyridinium chlorochromate [12], pyridinium dichromate [13], pyridinium fluorochromate [14], 2, 2'-bipyridinium chlorochromate [15], tripropylammonium fluorochromate [16] and tetramethylammonium fluorochromate (TMAFC) [17]. On the other hand in recent years organic reactions assisted by microwave and room temperature irradiation have gained special attention. The chief features of the microwave reactions are the enhanced selectivity, much improved reaction rates, milder reaction conditions and formation of cleaner products. These reactions are especially appealing as they can be carried out in open vessels thus avoiding the risk of development of high pressures in addition to the associated case of manipulation. In continuation of our ongoing work on development of highly efficient oxidation protocols, we observed that the oxidation of diols with Trialkylammonium fluorochromates(VI) $R_3NH[CrO_3F]$, ($R = CH_3, C_2H_5, C_3H_7$

and C_4H_9) (TriRAFC) under microwave and room temperature irradiation could be carried out much more quickly than using conventional techniques.

Results and Discussion

The results obtained with trialkylammonium fluorochromates(VI) $R_3NH[CrO_3F]$, ($R = CH_3, C_2H_5, C_3H_7$ and C_4H_9) (TriRAFC) at room temperature and under microwave radiations are very satisfactory and show that these new reagents as valuable additions to the existing oxidation agents. TriRAFC in dichloromethane under microwave and room temperature radiation oxidized diols in high yields (Tables 1 and 2).

Oxidations may also occur using only trialkylammonium fluorochromates in the absence of microwave irradiation but considerable improvements of both the yields and the corresponding reaction times are observed in the presence of the irradiation.

Neither carboxylic acids overoxidation products nor other by-products are formed upon oxidation of diols via trialkylammonium fluorochromates. Functional groups such as methyl that attached are inert to these reagents.

Trialkylammonium fluorochromates(VI) are easily prepared in high yields from chromium(VI) oxide, related trialkylamine and aqueous hydrofluoric acid (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 [18]. Moreover, during the reac-

Table 1. Oxidation via TriRAFC at room temperature

Substrate	Product	R=CH ₃		R=C ₂ H ₅		R=C ₃ H ₇		R=C ₄ H ₉	
		Time(min)	Yield(%)	Time(min)	Yield(%)	Time(min)	Yield(%)	Time(min)	Yield(%)
1 HO-CH ₂ -CH ₂ -OH	HO-CH ₂ -CHO	200	90	210	89	195	92	202	88
2 HO-CH ₃ -CH ₂ -CH ₂ -OH	HO-CH ₃ -CH ₂ -CHO	190	89	205	93	189	91	212	86
3 HO-(CH ₂) ₄ -OH	HO-(CH ₂) ₃ -CHO	165	88	175	90	166	91	171	89
4 CH ₃ -CH(OH)-CH(OH)-CH ₃	CH ₃ -CH(OH)-CO-CH ₃	170	91	185	87	174	90	184	87

Table 2. Oxidation via TriRAFC under Microwave irradiation

Substrate	Product	R = CH ₃		R = C ₂ H ₅		R = C ₃ H ₇		R = C ₄ H ₉	
		Time(min)	Yield (%)	Time(min)	Yield (%)	Time(min)	Yield (%)	Time(min)	Yield (%)
1 HO-CH ₂ -CH ₂ -OH	HO-CH ₂ -CHO	18	98	25	96	20	99	22	97
2 HO-CH ₃ -CH ₂ -CH ₂ -OH	HO-CH ₃ -CH ₂ -CHO	16	96	22	97	15	98	26	95
3 HO-(CH ₂) ₄ -OH	HO-(CH ₂) ₃ -CHO	10	93	12	95	8	97	15	94
4 CH ₃ -CH(OH)-CH(OH)-CH ₃	CH ₃ -CH(OH)-CO-CH ₃	10	96	15	94	9	98	17	95

tion, the colour of the oxidants change from orange to brown, thus providing a visual means for ascertaining the progress of the oxidations.

If the oxidizing agents are used in different ratio respect to the substrate (1:1.5, 1:2, 1:3) it is possible to achieve the oxidation of the two hydroxyl groups but it is impossible to achieve the conversion of primary diols to diacids under more drastic reaction conditions such as more time of heating of microwave irradiations or employing of higher boiling point solvent.

Trialkylammonium fluorochromates(VI) are soluble in water, dimethyl formamide, acetonitrile and acetone; these are less soluble in dichloromethane and only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

Experimental

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, ¹⁹F 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; 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 oxidant, chromium was determined after oxidizing 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. A Microsynth Milstone laboratory microwave oven has been used.

General Procedure for Synthesis of Trialkylammonium Fluorochromate (TriRAFC), R₃NH[CrO₃F] General Method

A 1 g (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 7 min the homogeneous solution was cooled to ca.-2 °C. To the resultant orange solution, trialkylamine (10 mmol) 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. The data of the reagents are:

Trimethylammonium Fluorochromate (TriMAFC), (CH₃)₃NH[CrO₃F]

Yield: (86%); mp 126 °C, C₃H₁₀CrFNO₃: C, 20.11; H, 5.58; N, 7.82. Found: C, 20.08; H, 5.64; N, 7.69. IR (KBr): 912 cm⁻¹ ν₁(A₁) or ν(CrO₃), 636 cm⁻¹ ν₂(A₁) or ν(Cr-F), 950 cm⁻¹ ν₄(E) or ν(CrO₃), Electronic absorption at 22026 cm⁻¹, corresponded to ¹A₂→¹E (ε = 174 M⁻¹cm⁻¹); 28735 m⁻¹ to ¹E→¹E (ε = 664 M⁻¹cm⁻¹) and 36231 cm⁻¹ to ¹A₂→¹E(ε = 1248 M⁻¹cm⁻¹). UV/Visible, ¹³C NMR, ¹H NMR and ¹⁹F 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 (TriE AFC), (C₂H₅)₃NH[CrO₃F]

Yield: (88%); mp 132 °C, C₆H₁₆CrFNO₃: C, 32.57; H, 7.23; N, 6.33. Found: C, 32.08; H, 7.54; N, 6.44. IR (KBr): 904 cm⁻¹ ν₁(A₁) or ν(CrO₃), 648 cm⁻¹ ν₂(A₁) or ν(Cr-F), 948 cm⁻¹ ν₄(E) or i(CrO₃), Electronic absorption at 22321 cm⁻¹, corresponded to ¹A₂→¹E (ε = 270 M⁻¹cm⁻¹); 28735 m⁻¹ to ¹E→¹E (ε = 845 M⁻¹cm⁻¹) and 36232 cm⁻¹ to ¹A₂→¹E (ε = 1233 M⁻¹cm⁻¹). UV/Visible, ¹³C NMR, ¹H NMR and ¹⁹F NMR were all consistent with the TriE AFC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution of TriE AFC in water was 3.45.

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

Yield: (98%); mp 142 °C, C₉H₂₂CrFNO₃: C, 41.06; H, 8.36; N, 5.32. Found: C, 41.22; H, 8.46; N, 5.22. IR (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.

Tributylammonium Fluorochromate (TriBAFC), (C₄H₉)₃NH[CrO₃F]

Yield: (84%); mp 134 °C, C₁₂H₂₈CrFNO₃: C, 47.21; H, 9.18; N, 4.59. Found: C, 46.92; H, 9.64; N, 5.20. IR (KBr): 914 cm⁻¹ ν₁(A₁) or i(CrO₃), 634 cm⁻¹ ν₂(A₁) or i(Cr-F), 950 cm⁻¹ ν₄(E) or ν(CrO₃), Electronic absorption at 22321 cm⁻¹, corresponded to ¹A₂→¹E (ε = 177 M⁻¹cm⁻¹); 28735 m⁻¹ to ¹E→¹E (ε = 701 M⁻¹cm⁻¹) and 35971 cm⁻¹ to ¹A₁→¹E (ε = 1314 M⁻¹cm⁻¹). UV/Visible, ¹³C NMR, ¹H NMR and ¹⁹F NMR were all consistent with the TriBAFC structure. The above procedure can be scaled up to larger quantities. The pH of 0.01 M solution of TriBAFC in water was 3.15.

General procedure for oxidation of diols:

To a stirred suspension of trialkylammonium fluorochromate (1 mmol) in dichloromethane (generally 5.0 mL), a solution of the substrate diol in the minimum amount of dichloromethane was added dropwise, the molar ratio of substrate to the oxidant being 1:1 in. The mixture was refluxed for the time showed in the table. [The completion of the reaction is followed by UV/Visible and TLC using ether/petroleum ether (60/40) as eluant]. 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. The separated compounds characterized and it is found

the product in that only one of the hydroxyl groups oxidized is the 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.

Under microwave conditions, all the above experiments were repeated (at 900W), and the mixture was irradiated for the time showed in the Table 2.

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