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Trialkylammonium chlorochromates (VI), $R_3NH[CrO_3Cl]$, ($R = CH_3, C_2H_5, C_3H_7$ and C_4H_9): New reagents for oxidation of some organic diols under microwave condition

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ABSTRACT

Trialkylammonium chlorochromates (VI), $R_3NH[CrO_3Cl]$, ($R = CH_3, C_2H_5, C_3H_7$ and C_4H_9) are mild and efficient reagents for the oxidation of diols in solution and in solution under microwave radiation. The easy procedure, simple work-up, short reaction times, and excellent yields are advantages of these reagents. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Diols;
Oxidation;
Oxidants;
Trialkylammonium
chlorochromates (VI);
Microwave;
Room temperature.

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 fluoro-chromate (TMAFC)^[11]. 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 and room temperature 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 chlorochromates (VI) $R_3NH[CrO_3Cl]$, ($R = CH_3, C_2H_5, C_3H_7$ and C_4H_9) (TriRACC) under microwave and room temperature irradiation could be carried out

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much more quickly than using conventional techniques.

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 NMR were carried out on a Bruker AVANCE DRX 500 spectrometer at 500, 125 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. 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 chlorochromate (TriRACC), R₃NH[CrO₃Cl]

Chromium (VI) oxide (1.0g, 10 mmol) was dissolved in water in a beaker and 6M hydrochloric acid (0.25 l cm³, 15 mmol) was added under stirring at 0°C. 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 precipice clear-orange crystalline solid was isolated by filtration, washed with petroleum ether (3×60cm³) and dried under vacuum for 2 h at room temperature.

The data of the reagents are

Trimethylammonium chlorochromate (TriMACC), (CH₃)₃NH[CrO₃Cl]

Yield: (59%); mp 126°C. Anal. Calcd. for C₃H₁₀ClCrNO₃ (%): C, 18.41; H, 5.115; N, 7.161.

Found: C, 18.52; H, 5.13; N, 7.17. IR (KBr): 902cm⁻¹ ν₁(A₁) or ν(CrO₃), 430cm⁻¹ ν₂(A₁) or ν(Cr-Cl), 948cm⁻¹ ν₄(E) or ν(CrO₃)cm⁻¹. UV/Visible and ¹H-NMR were all consistent with the TriMACC structure. Electronic absorption at 21881 cm⁻¹, corresponding to ¹A₂→¹E (ε = 360 dm³mol⁻¹ cm⁻¹); 28169cm⁻¹ to ¹E→¹E (ε = 906 dm³ mol⁻¹ cm⁻¹) and 3485cm⁻¹ to ¹A₂→¹A₁ (ε = 1157 dm³ mol⁻¹ cm⁻¹). The pH of 0.01 M solution of TriMACC in water was 2.7.

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

Yield: (54 %); mp 120°C. Anal. Calcd. for C₆H₁₆ClCrNO₃ (%): C, 30.315; H, 6.736; N, 5.894. Found: C, 30.29; H, 6.81; N, 5.82. IR (KBr): 900cm⁻¹ ν₁(A₁) or ν(CrO₃), 434cm⁻¹ ν₂(A₁) or ν(Cr-Cl), 950cm⁻¹ ν₄(E) or ν(CrO₃)cm⁻¹. UV/Visible and ¹H-NMR were all consistent with the TriEACC structure. Electronic absorption at 22075cm⁻¹, corresponding to ¹A₂→¹E (ε = 316 dm³mol⁻¹ cm⁻¹); 28169cm⁻¹ to ¹E→¹E (ε = 803 dm³ mol⁻¹ cm⁻¹) and 41152cm⁻¹ to ¹A₂→¹A₁ (ε = 1327 dm³ mol⁻¹ cm⁻¹). The pH of 0.01 M solution of TriEACC in water was 2.4.

Tripopylammonium chlorochromate (TriPACC), (C₃H₇)₃NH[CrO₃Cl]

Yield: (95%); mp 135°C. Anal. Calcd. for C₉H₂₂ClCrNO₃ (%): C, 38.64; H, 7.871; N, 5.008. Found: C, 37.93; H, 7.75; N, 4.88. IR (KBr): 901cm⁻¹ ν₁(A₁) or ν(CrO₃), 432cm⁻¹ ν₂(A₁) or ν(Cr-Cl), 949cm⁻¹ ν₄(E) or ν(CrO₃). Electronic absorption at 22123cm⁻¹, corresponded to ¹A₂→¹E (ε = 351 M⁻¹cm⁻¹); 28169cm⁻¹ to ¹E→¹E (ε = 793 M⁻¹cm⁻¹); 35087cm⁻¹ to ¹A₂→¹A₁ (ε = 1031 M⁻¹cm⁻¹) and 41493cm⁻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.

Tributylammonium chlorochromate (TriBACC), (C₄H₉)₃NH[CrO₃Cl]

Yield: (71%); mp 125°C. Anal. Calcd. for C₁₂H₂₈ClCrNO₃ (%): C, 44.79; H, 8.70; N, 4.35. Found: C, 44.59; H, 8.81; N, 4.38. IR (KBr): 898cm⁻¹ ν₁(A₁) or ν(CrO₃), 436cm⁻¹ ν₂(A₁) or ν(Cr-Cl), 940cm⁻¹ ν₄(E) or ν(CrO₃)cm⁻¹. UV/Visible and ¹H-NMR were

TABLE 1 : Oxidation via TriRACC in 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(%)
HO-CH ₂ -CH ₂ -OH	HO-CH ₂ -CHO	480	82	500	80	485	85	512	80
HO-CH ₂ -CH ₂ -CH ₂ -OH	HO-CH ₂ -CH ₂ -CHO	450	83	467	82	435	87	455	81
HO-(CH ₂) ₄ -OH	HO-(CH ₂) ₃ -CHO	400	79	420	75	395	82	405	80
CH ₃ -CH(OH)-CH(OH)-CH ₃	CH ₃ -CH(OH)-CO-CH ₃	420	85	430	83	418	89	435	87

TABLE 2 : Oxidation via TriRACC in microwave

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(%)
HO-CH ₂ -CH ₂ -OH	HO-CH ₂ -CHO	22	82	23	89	25	90	30	89
HO-CH ₂ -CH ₂ -CH ₂ -OH	HO-CH ₂ -CH ₂ -CHO	20	83	21	83	21	95	25	90
HO-(CH ₂) ₄ -OH	HO-(CH ₂) ₃ -CHO	19	79	20	89	17	85	20	84
CH ₃ -CH(OH)-CH(OH)-CH ₃	CH ₃ -CH(OH)-CO-CH ₃	19	85	21	83	20	95	25	82

all consistent with the TriBACC structure. Electronic absorption at 21881 cm⁻¹, corresponding to ¹A₂ → ¹E (ε = 336 dm³ mol⁻¹ cm⁻¹); 28089 cm⁻¹ to ¹E → ¹E (ε = 891 dm³ mol⁻¹ cm⁻¹) and 34965 cm⁻¹ to ¹A₂ → ¹A₁ (ε = 1178 dm³ mol⁻¹ cm⁻¹). The pH of 0.01 M solution of TriBACC in water was 2.8.

General procedure for oxidation of diols

To a stirred suspension of trialkylammonium chlorochromate (1 mmol) in dichloromethane (generally 5ml), 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 indicated in the TABLE 1. [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 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 355 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.

In microwave condition all of the above detailed repeated but the mixture was irradiated for the time indicated in the TABLE 2 by microwave radiation.

RESULTS AND DISCUSSION

The results obtained with trialkylammonium chlorochromates (VI) R₃NH[CrO₃Cl], (R = CH₃, C₂H₅, C₃H₇ and C₄H₉) (TriRACC) at room temperature and under microwave radiations are very satisfactory and show that these new reagents as valuable additions to the existing oxidation agents. TriRACC in dichloromethane under microwave and room temperature radiation oxidized diols in high yields (TABLE 1 and 2).

Oxidations may also occur using only trialkylammonium chlorochromates 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 chlorochromates. Functional groups such as methyl that attached are inert to these reagents.

Trialkylammonium chlorochromates (VI) are easily prepared in high yields from chromium (VI) oxide, related trialkylamine and aqueous hydrochloric acid (HCl) in a convenient molar ratio. The bright orange crystalline reagents can be stored in containers for long peri-

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ods without decomposition. The IR spectra of the reagents are similar to that of other halochromates.^[12] Moreover, during the reaction, 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 chlorochromates (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.

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