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Propyltriphenylphosphonium Chlorotrioxochromate(VI): A Mild and Efficient Oxidant for Oxidation of Organic Substrates

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The new mild chromium(VI) oxidizing agent, propyltriphenylphosphonium chlorochromate(VI), (PTriPPCC), was prepared and characterized. This new compound is effective in the oxidation of organic substrates specially alcohols to corresponding carbonyl compounds. The facile oxidation of triphenylphosphine to triphenylphosphine oxide by this reagent in CH_3CN provides a clear cut indicating for oxygen atom transfer mechanism.

Key Words: Chromium(VI), Oxidation, Alcohols, Propyltriphenylphosphonium chlorotrioxochromate, Organic substrate.

INTRODUCTION

In recent years, significant improvements were achieved by the use of new oxidizing agents[1-3] such as pyridinium dichromate (PDC)[4], pyridinium fluorochromate (PFC)[5], triphenylmethylposphonium chlorochromate[6], chromium trioxide-3,5-dimethylpyrazole complex (CrO_3 3,5-DMP)[7], tributylammonium chlorochromate (TriBACC)[8], 3,5-dimethylpyrazolium fluorochromate (DmpzHFC)[9], quinolinium fluorochromate (QFC)[10], 2,2'- bipyridinium chlorochromate (BiPCC)[11]. Many of above reagent be used the ammonium cation. Now we wish to use phosphonium cation as an oxidizing agent. In this research $PrPh_3P^+$ was used as a counter ion. There were some primary incentives for selection of $PrPh_3P^+$ as the counter ion. Firstly, quaternary ions such as phosphonium are often used as phase transfer catalysts. This could make propyltriphenylphosphonium chlorochromate(VI), $PrPh_3P[CrO_3Cl]$, (PTriPPCC) a more efficient and stronger oxidizing agent. This compound was used for quantitative oxidation of several organic substrates and is more efficient and has certain advantages over similar oxidizing agents in

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terms of the amount of oxidant and solvent required, short reaction times and high yields. Secondly, quaternary ions such as phosphonium are used as crystal growing agents. Hence using this counter ion, improves the quality of the PTriPPCC crystals.

EXPERIMENTAL

CrO_3 (Merck, p.a.) was used without further purification. Solvents were purified by standard methods. Melting points were determined in open capillaries on an Electrothermal 9200 apparatus and are not corrected. 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. ^1H and ^{13}C NMR were recorded on a Bruker Avance DRX 500 spectrometer at 500 and 125 MHz, respectively. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ^1H and ^{13}C NMR spectra were referenced to external $SiMe_4$. Chromium was estimated iodometrically. In the case of the reduced product of the oxidant, chromium was determined after oxidizing with acidic potassium peroxodisulfate ($K_2S_2O_8$) solution. The per cent composition of elements was obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Preparation of propyltriphenylphosphonium chlorotrioxochromate: Chromium(VI) oxide (1 g, 0.01 mol) was dissolved in water in a beaker and 30 % hydrochloric acid (15 mL, 0.298 mol) was added with stirring at 0 °C. To the resultant clear orange solution, Propyltriphenylphosphonium bromide (3.8 mg, 0.01 mol) was added with stirring to this solution over a period of 0.5 h and stirring was continued for 0.5 h at 0 °C. Within 5 min, a clear orange solution formed gave solid PTriPPCC, which was isolated by filtration. The solid was washed with hexane and dried under vacuum for 1 h. IR. (KBr, cm^{-1}): 902 cm^{-1} $\nu_1(A_1)$ or $\nu(CrO_3)$, 945 cm^{-1} $\nu_4(E)$ or $\nu(CrO_3)$, 431 cm^{-1} $\nu_2(A_1)$ or ν(Cr-Cl).UV/Visible ^{13}C NMR and ^1H NMR were all consistent with the PTriPPCC structure. Electronic transtions at 450 nm^{-1}, corresponding to $1a_2 \rightarrow 9e$ ($\varepsilon = 244\ M^{-1}\ cm^{-1}$); 363 nm^{-1} to $8e \rightarrow 9e$ ($\varepsilon = 466\ M^{-1}\ cm^{-1}$) and 274 nm^{-1} 1 to $12a_1 \rightarrow 9e$ ($\varepsilon = 904\ M^{-1}\ cm^{-1}$).

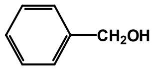
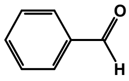
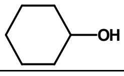
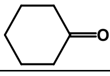
Oxidation of alcohols: General method: To PTriPPCC (0.001 mol) in CH_2Cl_2 (25 mL) was added the alcohol (0.001 mol) dissolved in a small amount of the solvent at room temperature. The mixture was stirred and refluxed for the time indicated in the Table-1 at room temperature, diluted with CH_2Cl_2 and filtered. Evaporation of solvent furnished the product. The molar ratio of substrate to oxidant was 1:1. The solution became homogeneous briefly before the black-brown reduced reagent precipitated. The progress of the reaction was monitored by TLC and UV/Vis spectrophotometry (at 363 nm).

RESULTS AND DISCUSSION

Propyltriphenylphosphonium chlorotrioxochromate can be easily prepared in good yield, quite stable when stored dry and in the absence of light and is active as oxidizing agents for the conversion of alcohols to carbonyl compounds.

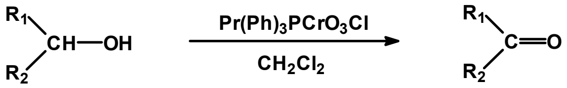
Granier *et al.*[12] have already linked the higher reactivities of $MCrO_3X$ ($M = K, Na, NR_4^+, NH_4^+$) and ($X = Cl, F, Br$), with the extent of symmetry about the Cr. They concluded that the inequality between the Cr-O and the Cr-X bonds is responsible for the higher reactivity. PTriPPCC appears to be a stronger reagent than the others. This could be due to its lower symmetry. It has also been found that this reagent has certain advantages over similar oxidizing agents in terms of the amounts of oxidant and solvent required and especially in the short reaction times required and in the higher yields of the product (Table-1)[13-16].

TABLE-1
OXIDATION OF ALCOHOLS AND POLYCYCLIC ARENES WITH PTriPPCC

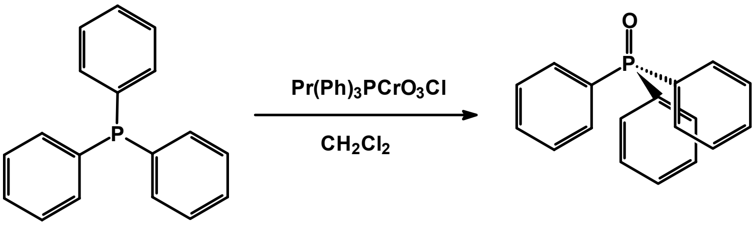
Substrate	Substrate/ oxidant ratio	Time (min)	Product	Yield (%)	b.p. (ºC)
1a n-C_3H_7-OH	1/1	120	**2a** n-C_2H_5-CHO	67	48-50
1b 2-C_3H_7-OH	1/1	80	**2b** 2-C_2H_5-CHO	88	55-57
1c n-C_4H_9-OH	1/1	90	**2c** n-C_3H_7-CHO	82	74-75
1d 2-C_4H_9-OH	1/1	60	**2d** 2-C_3H_7-CHO	94	79-80
1e n-C_5H_{11}-OH	1/1	90	**2e** n-C_4H_9-CHO	84	102
1f n-C_8H_{17}-OH	1/1	95	**2f** n-C_7H_{15}-CHO	90	170-172
1g 	1/1	47	**2g** 	95	177-179
1h 	1/1	5h	**2h** 	83	154-156

In conclusion, the lower acidity of this reagent, the ready preparation, its stability, nonhygroscopicity, the ease of the work up of the reaction mixture, reasonable yields of products and reaction time make propyltriphenylphosphonium chlorotriochromate(VI) a versatile and practical reagent for the oxidation of alcohols and a useful addition to the presently available bench reagents in organic synthesis. This reagent is easy to handle, can be weighed and has no hazardous effect.

Propyletriphenylphosphonium chlorotrioxochromate(IV) in dichloromethane also oxidizes primary and secondary alcohols to, respectively, the corresponding aldehydes or ketones in high yields (Table-1).



PTriPPCC and the results may also be useful in defining other related reactions. The reaction of triphenylphosphine with PTriPPCC (molar ratio of PPh_3: PTriPPCC = 1:1.1) in acetonitrile was carried out at room temperature and triphenylphosphine oxide was obtained in a quantitative yield. This provides a clear-cut example of an oxygen transfer reaction involving PTriPPCC and the result may also be useful in defining other related reactions.



During the reactions, the colour of the oxidant changes from orange to brown, providing visual means for ascertaining the progress of the oxidation. The results obtained with propyltriphenylphosphonium chlorotrioxochromate(VI) are satisfactory and shows the new reagent as a valuable addition to the existing oxidizing agents.

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REFERENCES

1. G. Marier, H.P. Reisenauer and M.D. Marco, *Angew. Chem. Int. Ed. Engl.*, **38**, 108 (1999).
2. A. Bhandari, P.K. Sharma and K.K. Banerji, *Indian J. Chem.*, **40A**, 470 (2001).
3. S. Meenahshisundaram and R. Soctaungam, *Collect. Czec. Chem. Commun.*, **66**, 877 (2001).
4. M.Z. Kassaee, S.Z. Sayyed-Alangi and H. Sajjadi-Ghotbabadi, *Molecules*, **9**, 825 (2004).
5. M.N. Bhattacharjee, M.K. Chaudhuri, H.S. Dasgupta and N. Roy, *Synthesis*, 588 (1982).
6. A.R. Hajipour, L. Khazdooz and A.E. Ruoho, *J. Iranian Chem. Soc.*, **2**, 315 (2005).
7. E.J. Corey and G.W. Fleet, *Tetrahedron Lett.*, **14**, 4499 (1973).
8. S. Ghammamy and S.A. SeyedSadjadi, *J. Serb. Chem. Soc.*, **70**, 1243 (2005).
9. R. Srinivasan, C.V. Ramesh, W. Madhulatha and K. Balasubramanian, *Indian J. Chem.*, **35B**, 480 (1996).
10. U. Bora and M.K. Chaudhuri, *Tetrahedron*, **57**, 2445 (2001).
11. F.S. Guziec and F.A. Luzzio, *Synthesis*, **12**, 691 (1980).
12. W. Granier, S. Vilminot and J.D. Vidal, *J. Fluorine Chem.*, **19**, 123 (1981).
13. K.M. Harmon, I. Gennick and S.L. Madeira, *J. Phys. Chem.*, **78**, 2585 (1974).
14. M.N. Bahttacharjee, M.K. Chauduri and H.S. Dasgupta, *Synthesis*, 588 (1982).
15. R. Srinivasan, P. Stanly and K. Balasubramanian, *Synth. Commun.*, **27**, 2057 (1997).
16. J.C. Collins, W.W. Hess and F.J. Frank, *Tetrahedron Lett.*, **9**, 3363 (1968).

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