Asian Journal of Chemistry Vol. 17, No. 4 (2005), 2137–2142

Synthesis of Dodecyltrimethylammonium Bromochromate: An Improved Cr(VI)-Oxidant Reagent for Organic Substrates

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Orange-brown crystalline dodecyltrimethylammonium bromochromate, $(C_{12}H_{25})N(CH_3)_3[CrO_3Br]$, is easily prepared in a nearly quantitative yield by the interaction of dodecyltrimethylammonium bromide with CrO_3 in 1 : 1 molar ratio. This reagent is versatile for the effective and selective oxidation of organic substrates, in particular for alcohols, under mild conditions. The reagent in CH_2Cl_2 readily oxidizes primary and secondary alcohols to the corresponding carbonyls, carbohydrate to ketosugre, anthracene and phenanthrene to anthraquinone and phenanthraquinone, respectively.

Key Words: Oxidant, Chromium(VI) reagent, Dodecyltrimethylammonium bromochromate, Oxidation, Organic substrates.

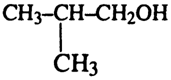
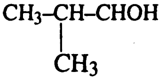
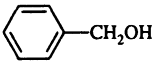
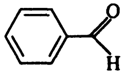
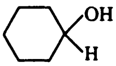
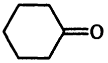
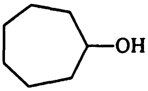
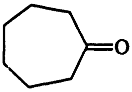
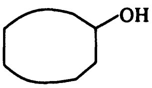
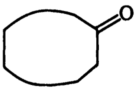
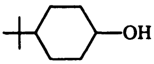
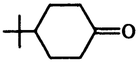
INTRODUCTION

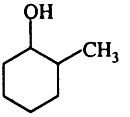
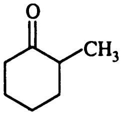
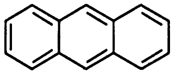
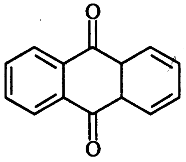
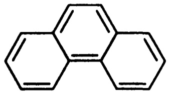
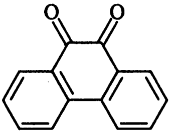
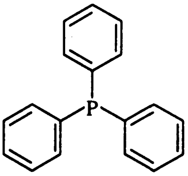
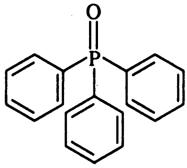
The important prerequisites for an oxidant to be useful are its mildness, versatility, selectivity and operational simplicity. Considering these, development of oxidizing agents based upon higher-valent transition metal oxo derivatives has been the objective of many research laboratories and a host of such reagents derived from ruthenium, osmium, iron, manganese, molybdenum, vanadium and chromium have all proved 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], pyridinium fluorochromate[5], quinolinium dichromate[6], caffeinilium chlorochromate[7], quinolinium chlorochromate[8], isoquinolinium fluorochromate[9] and tetramethylammonium fluorochromate[10]. In this paper, the synthetic potential of dodecyltrimethylammonium bromochromate, $(C_{12}H_{25})N(CH_3)_3[CrO_3Br]$, (DTMABC) is investigated and it has been found that this reagent has certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, easier working up and high yields. Further, DTMABC does not react with acetonitrile, which is a suitable medium for studying kinetics and mechanism.

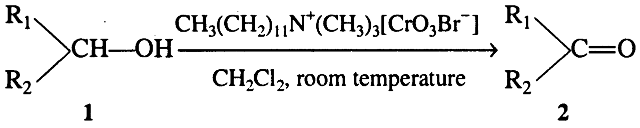
RESULTS AND DISCUSSION

The results obtained with DTMABC are very satisfactory and show the new reagent as a valuable addition to the existing oxidizing agents. DTMABC in dichloromethane oxidizes primary **(1a–h)** and secondary **(3a–i)** alcohols to the corresponding aldehydes **(2a–h)** or ketones **(4a–i)** in high yields (Table-1).

TABLE-1
OXIDATION OF ALCOHOLS AND POLYCYCLIC ARENES WITH DTMABC

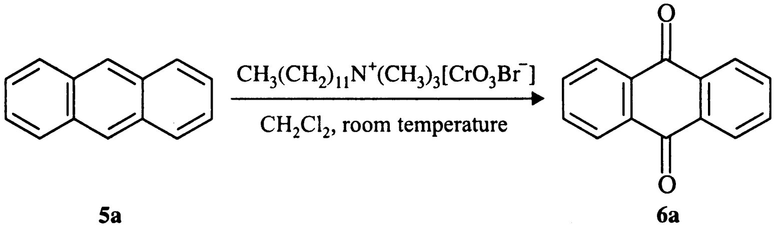
Substrate	Substrate/ oxidant ratio	Time (min)	Product	Yield (%)	m.p. (°C)	b.p. (°C)
1a $n\text{-}C_3H_7\text{—}OH$	1/1	160	**2a** $n\text{-}C_2H_5\text{—}CHO$	90		48–50
1b $n\text{-}C_4H_9\text{—}OH$	1/1	150	**2b** $n\text{-}C_3H_7\text{—}CHO$	90		74–75
1c $n\text{-}C_5H_{11}\text{—}OH$	1/1	65	**2c** $n\text{-}C_4H_9\text{—}CHO$	90		102
1d $n\text{-}C_6H_{13}\text{—}OH$	1/1	40	**2d** $n\text{-}C_5H_{11}\text{—}CHO$	90		129–131
1e  $CH_3\text{-}\underset{\substack{\vert\\ CH_3}}{C}H\text{-}CH_2OH$	1/1	75	**2e**  $CH_3\text{-}\underset{\substack{\vert\\ CH_3}}{C}H\text{-}CHOH$	89		63–64
1f $n\text{-}C_8H_{17}\text{—}OH$	1/1	50	**2f** $n\text{-}C_7H_{15}\text{—}CHO$	92		170–172
1g $n\text{-}C_{11}H_{23}\text{—}OH$	1/1	50	**2g** $n\text{-}C_{10}H_{21}\text{—}CHO$	75		110–113
1h 	1/1	45	**2h** 	92		177–179
3a $2\text{-}C_3H_7\text{—}OH$	1/1	170	**4a** $2\text{-}C_3H_6O$	93		56.2
3b $3\text{-}C_7H_{15}\text{—}OH$	1/1	80	**4b** $3\text{-}C_7H_{14}O$	93		146–148
3c $2\text{-}C_8H_{17}\text{—}OH$	1/1	55	**4c** $2\text{-}C_8H_{16}O$	95		172–173
3d $2\text{-}C_{11}H_{23}\text{—}OH$	1/1	70	**4d** $2\text{-}C_{11}H_{22}O$	90		230–234
3e 	1/1	150	**4e** 	89		154–156
3f 	1/1	35	**4f** 	90		179–181
3g  Cyclododecanol	1/1	40	**4g**  Cyclododecanone	90	50–61	
3h 	1/1	430	**4h** 	89	47–50	162–163

3i		1/1	153	**4i**		90	
5a		1/2	63	**6a**		90	284–285
5b		1/2	80	**6b**		67	208–210
7a		1/1.1	7	**8a**		90	156–157



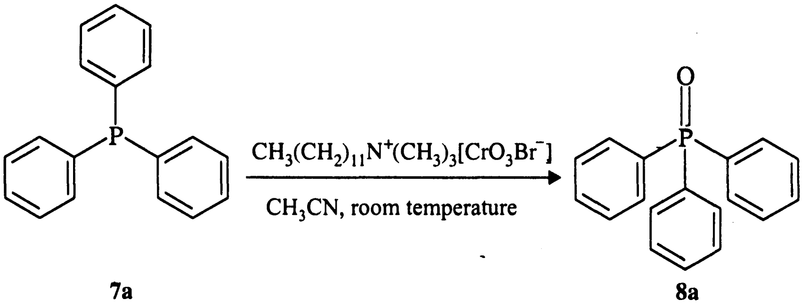
Scheme-1

DTMABC in dichloromethane also oxidizes anthracene (**5a**) and phenanthrene (**5b**) to anthraquinone (**6a**) and phenanthraquinone (**6b**) in 90 and 67% yields respectively. This reagent works as efficiently as activated manganese dioxide or Collins reagent[11].



Scheme-2

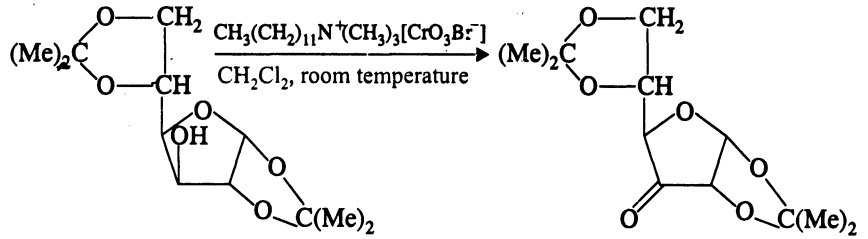
The reaction of triphenylphosphine with DTMABC (molar ratio of PPh_3: DTMABC = 1 : 1.1) in acetonitrile was carried out at room temperature and triphenylphosphine oxide was obtained in a quantitative yield. This provides a clear-cut example of an oxygen transfer reaction involving DTMABC and the result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



7a **8a**

Scheme-3

DTMABC has also been used for oxidation of carbohydrates such as 1,2:5,6-di-O-isopropylidine-α-D-glucofuranose (**9a**) to its relative ketosugar (**10a**) like as pyridinium chlorochromate[12] but in 90% yield, in 50 min and by use of the equimolar ratio of the reagent.



9a **10a**

Scheme-4

DTMABC is easily prepared in 96% yield from chromium(VI) oxide and dodecyltrimethylammonium bromide in a molar ratio of 1 : 1. The orange-brown crystalline reagent can be stored in polyethylene containers for long periods without decomposition. The IR spectrum is similar to that of other bromochromates[13].

DTMABC is soluble in water, dimethylformamide, acetonitrile, acetone and dichloromethane. It is only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

EXPERIMENTAL

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-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 ^{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 peroxodisulfate ($K_2S_2O_8$) solution. The per cent compositions of carbon, hydrogen and nitrogen were obtained from the microanalytical laboratories, Department of Chemistry, OIRC, Tehran, Iran.

Preparation of dodecyltrimethylammonium bromochromate (DTMABC)

A measured amount of chromium(VI) oxide (CrO_3: 1.07 g, 10.7 mmol) was dissolved in acetonitrile (25 mL) in a beaker and stoichiometric amount of dodecyltrimethylammonium bromide, $CH_3(CH_2)_{11}(CH_3)_3NBr$ (3.30 g, 10.7 mmol) was added with stirring at room temperature, within 5 min a clear orange-brown solution resulted. Upon refrigerating, solid DTMABC was form which was isolated by filtration. Washed by dry isopropanol and diethyl ether, pressed between the folds of a filter paper and dried in vacuum for 1 h. Slow evaporation of the concentrated solution of $CH_3(CH_2)_{11}(CH_3)_3N[CrO_3Br]$ in acetonitrile gave suitable crystals after one week. Yield 4.19 g (96%); m.p. 151°C. Anal. (%), Calcd. for $C_{15}H_{34}BrCrNO_3$: C, 44.079; H, 8.326; N, 3.428; Found: C, 43.78; H, 8.12; N, 3.26. IR (KBr, cm^{-1}): 904 $\nu_1(A_1)$ or $\nu(CrO_3)$, 394 $\nu_2(A_1)$ or ν(Cr—Br), 937 $\nu_4(E)$ or $\nu(CrO_3)$. UV-Visible, ^{13}C NMR and ^1H NMR were all consistent with the DTMABC structure.

The above procedure can be performed on a 250 g scale without any difficulty.

General procedure for oxidation of organic substrates with dodecyltrimethylammonium bromochromate (DTMABC)

To a stirred suspension of DTMABC (4.1 g) in dichloromethane (generally 5 mL), a solution of the substrate in the minimum amount of dichloromethane was added dropwise, the molar ratio of substrate to the oxidant being 1 : 1 in the case of alcohols **(1, 3)** and 1 : 2 in the case of arenes **(5)** (Table-1). The mixture was refluxed for the time indicated in the table. [The completion of the reaction was followed by UV-Visible and TLC using ether : petroleum ether (60 : 40) as eluant]. The mixture was 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.

The progress of the reactions was monitored and checked by UV-Visible spectrophotometry. The amount of the oxidant during the reaction was measured spectrophotometrically at 410 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 the cell. The reaction mixtures remained homogeneous in the solvent system used.

Reaction of DTMABC with triphenylphosphine

The reaction was performed in all nitrogen atmosphere in a dry 100 mL round-bottomed flask and under efficient stirring. To a vigorously stirred solution of 1.5 g (5.7 mmol) of triphenylphosphine in 35 mL of acetonitrile, 2.56 g (6.28 mmol) of DTMABC was added in two installments in about 1 min, maintaining the substrate : oxidant ratio at 1 : 1.1. An exothermic reaction set in instantaneously, and was complete in 7 min. The solution was cooled and the mother liquor and the washings, after separation of reduced DTMABC product by centrifugation, was filtered thorough a short silica gel column (7 × 2 cm^2). The contents of the column were throughly washed with ether (3 × 35 cm^3) and filtered. The combined filtrates were evaporated on a steam bath and the product was characterized as triphenylphosphine oxide by elemental analyses and IR spectral studies. Yield of $OPPh_3$: 1.42 g (90%). m.p.: found 155°C (Lit. m.p. 156–157°C).

Oxidation of anthracene with DTMABC

In a dry round-bottomed flask, 0.178 g (1 mmol) of anthracene was dissolved in 10 mL of CH_2Cl_2. To the solution, 0.81 g (2 mmol) of DTMABC was added and refluxed for 1 h. The progress of the reaction was monitored by TLC. The reaction mixture was concentrated using a short pad of celite to trap the reduced product of the reagent and washed thoroughly with diethyl ether. The filtrate was evaporated in an evaporator to give a crude product, which was purified by column chromatography over a short pad of silica gel using ethyl acetate-hexane (1 : 9) as eluent. 9,10-anthraquinone was obtained as a yellow crystalline compound having m.p. 283°C (lit. m.p. 282–285°C). Yield of the compound was 0.18 g (90%).

ACKNOWLEDGEMENTS

The authors thank Dr. A.R. Mahjoub and Mr. A. Hashemzadeh for valuable discussions.

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(*Received*: 17 March 2004; *Accepted*: 20 May 2005) AJC-4229