

Tributylammonium chlorochromate, (C₄H₉)₃NH[CrO₃Cl] (TriBACC): A new, mild and stable oxidant for organic substrates

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Abstract: A mild and stable new chromium(VI) reagent from tributylamine is described. Orange crystalline tributylammonium chlorochromate(VI), (C₄H₉)₃NH[CrO₃Cl], (TriBACC), is easily prepared in a nearly quantitative yield by the interaction of tributylamine with CrO₃ and hydrochloric acid in a 1:2:2 mole ratio. This reagent is a versatile reagent for the effective and selective oxidation of organic substrates, in particular for alcohols, under mild conditions.

Keywords: oxidant, chromium(VI) reagent, tributylammonium chlorochromate, oxidation, organic substrates.

INTRODUCTION

The development of oxidizing agents based upon higher-valent transition metal oxo derivatives has been a subject of research in many laboratories and a host of such reagents derived from ruthenium, osmium, iron, manganese, molybdenum, vanadium and chromium have all proven 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 caffeinium chlorochromate,⁷ quinolinium chlorochromate,⁸ isoquinolinium fluorochromate⁹ and tetramethylammonium fluorochromate.¹⁰ In this study, the synthetic potential of tributylammonium chlorochromate, (C₄H₉)₃NH[CrO₃Cl], (TriBACC) were investigated. It was 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. Furthermore, tributylammonium chlorochromate does not re-

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act with acetonitrile, which is a suitable medium for studying kinetics and mechanism.

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. ¹H and ¹³C-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 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 potassium peroxodisulfate (K₂S₂O₈) solution. The chloride content was determined gravimetrically as AgCl. The percent composition of carbon, hydrogen and nitrogen were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

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

Chromium(VI) oxide (15.0 g, 0.15 mol) was dissolved in water in a beaker and 6 M hydrochloric acid (25 cm³, 0.3 mol) was added under stirring at 0 °C. To the resultant clear orange solution, tributylamine (71.29 cm³, 0.3 mol) was added dropwise under stirring over a period of 0.5 h and the stirring was continued for 0.5 h at 0 °C. The precipitated orange solid was isolated by filtration, washed with petroleum ether (3 x 60 cm³) and dried under vacuum for 2 h at room temperature. Yield: 45.81 g (95 %); mp 165 °C. Calcd. for C₁₂H₂₈ClCrNO₃: C, 44.79; H, 8.70; N, 4.35. Found: C, 44.31; H, 8.53; N, 4.19. IR (KBr): 913 cm⁻¹ ν₁(A₁) or ν(CrO₃), 432 cm⁻¹ ν₂(A₁) or ν(Cr-Cl), 970 cm⁻¹ ν₄(E) or ν(CrO₃) cm⁻¹. UV/Visible and ¹H-NMR were all consistent with the TriBACC structure. Electronic absorption at 22026 cm⁻¹, corresponding to ¹A₂ → ¹E (ε = 145 dm³mol⁻¹ cm⁻¹); 28985 cm⁻¹ to ¹E → ¹E (ε = 577 dm³ mol⁻¹ cm⁻¹) and 43103 cm⁻¹ to ¹A₂ → ¹A₁ (ε = 1081 dm³ mol⁻¹ cm⁻¹). ¹H-NMR (500 MHz, CD₃CN): δ = 1.2 (t, 3H, -CH₃), δ = 1.6 (m, 4H, -CH₂-CH₂-), δ = 2.7 (t, 2H, -CH₂-), δ = 7.5 ppm (s, 1H, -NH).

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

General procedure for oxidation of organic substrates with tributylammonium chlorochromate

To a stirred suspension of tributylammonium chlorochromate (3.3 g) in dichloromethane (generally 5 cm³), a solution of the substrate in the minimum amount of dichloromethane was added dropwise, the mole 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**) (See Table I). The mixture was refluxed for the time indicated in the table. The completion of the reaction was followed by UV/Visible spectroscopy and 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 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 consumed during the reaction was measured spectrophotometrically at 345 nm. A very small magnetic stirrer was designed in the spectrophotometer cell compartment (10 mm quartz cell) just at the bottom of sample cell to enable the solution under study in the cell to be stirred. The reaction mixtures remained homogenous in the solvent system employed.

Reaction of TriBACC with triphenylphosphine

The reaction was performed under a nitrogen atmosphere in a dry 100 ml round bottomed flask under efficient stirring. To a vigorously stirred solution of 1.5 g (5.7 mmol) of triphenylphosphine in 35 cm³ of acetonitrile, 2.02 g (6.28 mmol) of TriBACC was added in two instalments in about one

minute, maintaining the substrate: oxidant ratio 1:1.1. An exothermic reaction started instantaneously and was completed in 10 min. The solution was cooled and the mother liquor and the washings, after separation of the reduced TriBACC product by centrifugation, was filtered through a short silica gel column (7 x 2 cm²). The contents of the column were thoroughly washed with ether (3 x 35 cm³) and filtered. The combined filtrates were evaporated on a steam bath, and the product was characterised as triphenylphosphine oxide by elemental analyses and IR spectral studies. Yield of OPPh₃: 1.48 g (93 %), mp 156 °C (lit. mp 156–157 °C).¹¹

Oxidation of anthracene with TriBACC

In a dry round bottomed flask, 0.178 g (1 mmol) of anthracene was dissolved in 10 cm³ of CH₂Cl₂. To the solution, 0.64 g (2 mmol) of TriBACC was added and refluxed for 4 h. The progress of the reaction was monitored by TLC. The reaction mixture was filtered 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 the eluent. 9,10-Anthraquinone was obtained as a yellow crystalline compound having mp 283 °C (lit. mp 282–285 °C).⁹ Yield of the compound **6a** was 0.13 g (65 %).

RESULTS AND DISCUSSION

Tributylammonium chlorochromate was easily prepared in 95 % yield from chromium(VI) oxide, tributylamine and aqueous 6 M hydrochloric acid in a mole ratio of 1:2:2. The bright orange crystalline reagent can be stored in polyethylene containers for long periods without decomposition. The IR spectrum is similar to that of other chlorochromates.¹² Tributylammonium chlorochromate is soluble in water, dimethylformamide, acetonitrile, acetone and dichloromethane. It is only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

The results obtained with tributylammonium chlorochromate are very satisfactory and show the new reagent to be a valuable addition to existing oxidizing agents.

Tributylammonium chlorochromate in dichloromethane oxidizes primary (**1a-h**) and secondary alcohols (**3a-i**) to the corresponding aldehydes (**2a-h**), or ketones (**4a-i**) in high yields (Scheme 1, Table I).

TABLE I. Oxidation of alcohols and polycyclic arenes with TriBACC

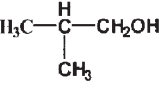
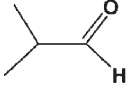
	Substrate	Time/min	Product	Yield/%	M.p./°C	B.p./°C
1a	<i>n</i> -C ₃ H ₇ -OH	180	2a C ₂ H ₅ -CHO	90		48–50
1b	<i>n</i> -C ₄ H ₉ -OH	165	2b <i>n</i> -C ₃ H ₇ -CHO	88		74–75
1c	<i>n</i> -C ₅ H ₁₁ -OH	130	2c <i>n</i> -C ₄ H ₉ -CHO	85		102
1d	<i>n</i> -C ₆ H ₁₃ -OH	110	2d <i>n</i> -C ₅ H ₁₁ -CHO	85		129–131
1e		165	2e 	90		63–64
1f	<i>n</i> -C ₈ H ₁₇ -OH	110	2f <i>n</i> -C ₇ H ₁₅ -CHO	93		170–172
1g	<i>n</i> -C ₁₁ H ₂₃ -OH	85	2g <i>n</i> -C ₁₀ H ₂₁ -CHO	85		110–113

TABLE I. Continued

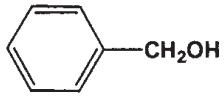
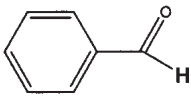
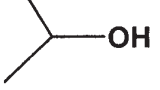
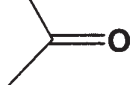
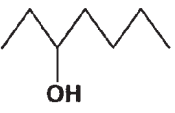
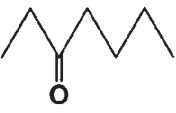
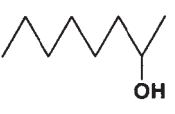




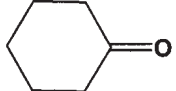
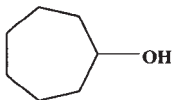
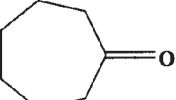
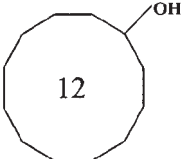
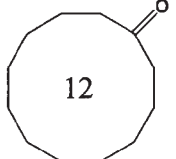
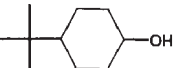

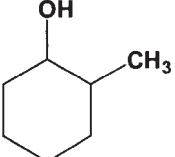
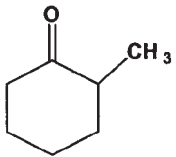
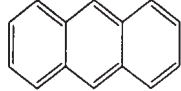
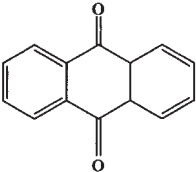
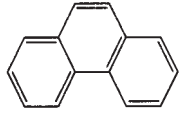
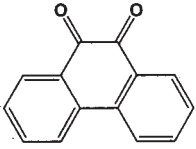
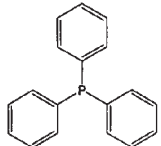
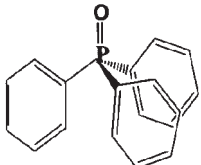
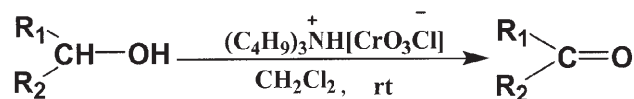
	Substrate	Time/min	Product	Yield/%	M.p./°C	B.p./°C
1h		45	2h 	95		177–179
3a		130	4a 	90		55–57
3b		120	4b 	94		146–148
3c		115	4c 	93		172–173
3d		80	4d 	88		230–234
3e		200	4e 	78		154–156
3f		120	4f 	93		179–181
3g		135	4g 	92	50–61	
3h		14h	4h 	80	47–50	
3i		165	4i 	92		162–163

TABLE I. Continued

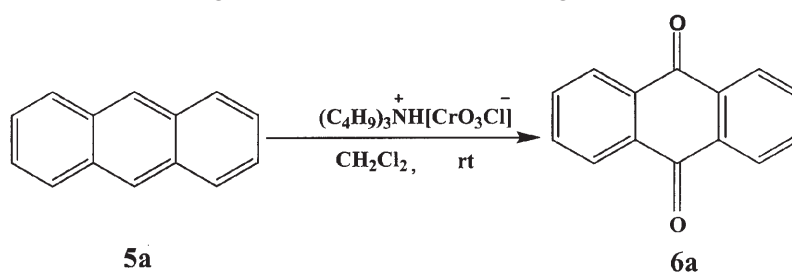
Substrate	Time/min	Product	Yield/%	M.p./°C	B.p./°C
 5a	4h	 6a	65	284–285	
 5b	4h	 6b	63	208–210	
 7a	10	 8a	93	156–157	

The mole ratio of substrate to the oxidant 1:1 in the case of alcohols (1, 3) and 1:2 in the case of arenes (5)



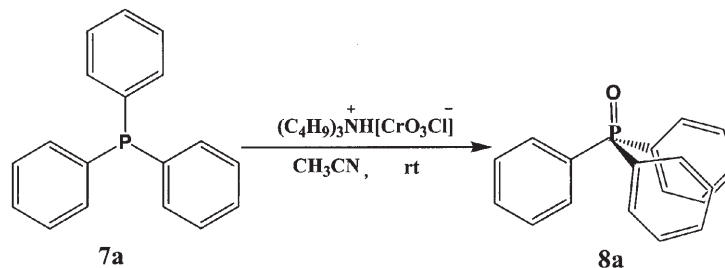
Scheme 1.

Tributylammonium chlorochromate in dichloromethane also oxidizes anthracene (5a) and phenanthrene (5b) to anthraquinone (6a) and phenanthraquinone (6b) in 65 % and 63 % yields, respectively (Scheme 2). This reagent works as efficiently as activated manganese dioxide or Collins reagent.¹³



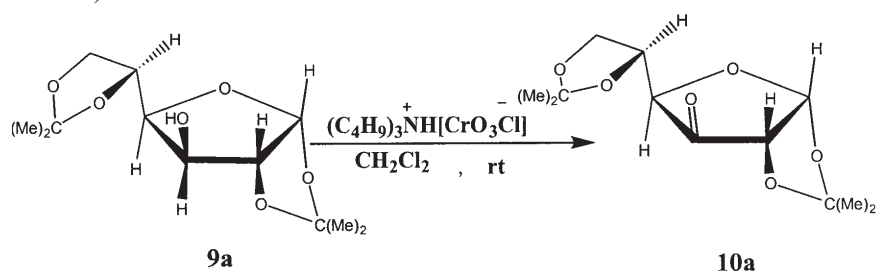
Scheme 2.

The reaction of triphenylphosphine with TriBACC (mole ratio of PPh₃: TriBACC = 1:1.1) in acetonitrile was carried out at room temperature and triphenylphosphine oxide was obtained in a quantitative yield (Scheme 3). This provides, as expected, a clear-cut example of an oxygen transfer reaction involving TriBACC, and the result may also be useful in defining other related reactions.



Scheme 3.

Tributylammonium chlorochromate has also been used for the oxidation of carbohydrates, such as 1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose (**9a**) to its relative ketosugar (**10a**), as was the case with pyridinium chlorochromate,¹⁴ but in 78 % compared to 63 % yield, and with the use of an equimolar ratio of the reagent (Scheme 4).



Scheme 4.

CONCLUSION

It was also found that the studied reagent has certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, and especially in the short reaction times required and in higher product yields.^{5,9}

Because of the stability and solubility of TriBACC, the reactions can be performed at room temperature and the separation of the products is facile. During the reactions, the color of the oxidant changes from orange to brown, providing visual means for ascertaining the progress of the oxidation. The mechanism for the present oxidation is still unclear. However, it is assumed that the oxidation mechanism is similar to that of other chlorochromates. In addition this oxidant and the oxidation conditions can be used for the synthesis of highly functionalized molecules.

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ИЗВОД

ТРИБУТИЛАМОНИЈУМ-ХЛОРОХРОМАТ – НОВО БЛАГО И СТАБИЛНО
ОКСИДАЦИОНО СРЕДСТВО ЗА ОРГАНСКЕ СУПСТРАТЕ

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Описан је нов благ и стабилан реагенс добијен од хрома(VI) и трибутиламина. Међусобним дејством трибутиламина, CrO₃ и хлороводоничне киселине у молском односу 1:2:2 лако се добија оранж кристалиничан трибутиламонијум-хлорохромат(VI), (C₄H₉)₃NH[CrO₃Cl], (TriBACC), у скоро квантитативном приносу. Производ је многострани реагенс за ефикасну и селективну оксидацију органских супстрата, нарочито алкохола, у благим условима.

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