

## Synthesis and Characterization of Four New Trialkylammonium Sulfatotrioxochromates, $[\text{R}_3\text{NH}]_2\text{CrO}_3\text{SO}_4$ , ( $\text{R} = \text{Me, Et, } n\text{-Pr, } n\text{-Bu}$ )

MARYAM HAJIGHAHRAMANI<sup>†</sup>, RASHID ZAMANPOOR<sup>†</sup>, SHAHRIARE GHAMMAMY\*,  
KHEYROLLAH MEHRANI<sup>†</sup>, TAHMINEH BANIBAIRAMI<sup>†</sup>, RAHMATTOLLAH RAHIMI<sup>‡</sup> and SINA ASILI<sup>§</sup>

*Department of Chemistry, Faculty of Science,  
Imam Khomeini International University, Ghazvin, Iran  
E-mail: shghamami@ikiu.ac.ir; shghamamy@yahoo.com*

The new mild chromium(VI) oxidizing agents *i.e.*, trialkylammonium sulfatotrioxochromates (TriRASC), were prepared and characterized. These reagents are suitable for oxidizing various primary and secondary alcohols to their corresponding carbonyl compounds and anthracene to anthraquinone. Orange solids (TriRASC), is easily synthesized by the reaction of chromium(VI) oxide:trialkylamine: in 1:2 molar ratios and sufficient sulfuric acid. These reagents are versatile reagents for the effective and selective oxidation of organic substrates, in particular for alcohols, under mild conditions.

**Key Words: Chromium(VI), Oxidation, Organic substrate, Alcohols, Trialkylammonium sulfatotrioxochromates.**

### INTRODUCTION

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, significant improvements were achieved by the use of new oxidizing agents<sup>1-3</sup>, such as 3-carboxypyridinium chlorochromate<sup>4</sup>, pyridinium fluorochromate<sup>5</sup>, quinolinium dichromate<sup>6</sup>, caffeinilium chlorochromate<sup>7</sup>, quinolinium chlorochromate<sup>8</sup>, isoquinolinium chlorochromate<sup>9</sup> and tetramethylammonium fluorochromate<sup>10</sup>. These oxidants are mostly used for oxidation of alcohols to their corresponding aldehydes and ketones<sup>11-27</sup>. In this report, we introduce trialkylammonium sulfatotrioxo-chromates (TriRASC), that have certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields.

### EXPERIMENTAL

Melting points were obtained on an Electrothermal 9100 apparatus. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Bruker DRX-500 in CDCl<sub>3</sub> solutions.

<sup>†</sup>Department of Chemistry, Faculty of Science, Islamic Azad University, Ardabil Branch, Ardabil, Iran.

<sup>‡</sup>Faculty of Chemistry, Iran University of Science and Technology, Tehran, Iran.

<sup>§</sup>Babasafari Student Research Center, Ardabil Branch, Ardabil, Iran.

The UV/Visible measurements were made on an Uvicon model 922 spectrometer. All separations and quantization of alcohols and aldehydes were performed using a Philips 4410 gas chromatograph. All reagents and solvents are of reagent grades.

**Preparation:** CrO<sub>3</sub> was dissolved in water in a beaker and sulfuric acid was added with stirring at 0 °C, then a stoichiometric amount of trialkylamine was added dropwise with stirring to this solution over a period of 7 h at 0 °C. The solid was isolated by filtration then was washed with hexane and dried under vacuum for 1 h.

**Trimethylammonium sulfatotrioxochromate (TriMASC) [N(CH<sub>3</sub>)<sub>3</sub>H]<sub>2</sub>CrO<sub>3</sub>SO<sub>4</sub>:** C<sub>6</sub>H<sub>20</sub>N<sub>2</sub>O<sub>7</sub>SCr: Calcd. (%) C, 22.78; H, 6.329; N, 8.86. Found (%) C, 23.82; H, 6.51; N, 9.19. IR. (KBr, cm<sup>-1</sup>): 902 ν<sub>1</sub>(A<sub>1</sub>) or ν(CrO<sub>3</sub>), 945 ν<sub>4</sub>(E) or ν(CrO<sub>3</sub>), 1133 ν<sub>2</sub>(A<sub>1</sub>) or ν(S-O). UV/Visible <sup>13</sup>C NMR and <sup>1</sup>H NMR were all consistent with the TriMASC structure. Electronic at 450 nm<sup>-1</sup>, corresponding to 1a<sub>2</sub>→9e (ε = 228 M<sup>-1</sup> cm<sup>-1</sup>); 362 nm to 8e→9e (ε = 733 M<sup>-1</sup> cm<sup>-1</sup>) and 282 nm<sup>-1</sup> to 12a<sub>1</sub>→9e (ε = 1238 M<sup>-1</sup> cm<sup>-1</sup>).

**Triethylammonium sulfatotrioxochromate (TriEASC) [N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>H]<sub>2</sub>CrO<sub>3</sub>SO<sub>4</sub>:** C<sub>12</sub>H<sub>32</sub>N<sub>2</sub>O<sub>7</sub>SCr: Calcd. (%) C, 36.00; H, 8.00; N, 7.00. Found (%) C, 36.82; H, 8.17, N, 7.28. IR. (KBr, cm<sup>-1</sup>): 898 ν<sub>1</sub>(A<sub>1</sub>) or ν(CrO<sub>3</sub>), 950 ν<sub>4</sub>(E) or ν(CrO<sub>3</sub>) 1173 ν<sub>2</sub>(A<sub>1</sub>) or ν(S-O). UV/Visible was all consistent with the TriEASC structure. Electronic absorption at 452 nm, corresponding to 1a<sub>2</sub>→9e (ε = 161 M<sup>-1</sup> cm<sup>-1</sup>); 364 nm to 8e→9e (ε = 737 M<sup>-1</sup> cm<sup>-1</sup>) and 261 nm to 12a<sub>1</sub>→9e (ε = 1683 M<sup>-1</sup> cm<sup>-1</sup>).

**Tripropylammonium sulfatotrioxochromate (TriPASC) [N(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>H]<sub>2</sub>CrO<sub>3</sub>SO<sub>4</sub>:** C<sub>18</sub>H<sub>44</sub>N<sub>2</sub>O<sub>7</sub>SCr: Calcd. (%) C, 44.62; H, 9.09; N, 5.78. Found (%) C, 45.73; H, 9.31; N, 5.98. IR. (KBr, cm<sup>-1</sup>): 902 ν<sub>1</sub>(A<sub>1</sub>) or ν(CrO<sub>3</sub>), 948 ν<sub>4</sub>(E) or ν(CrO<sub>3</sub>) 1097 ν<sub>2</sub>(A<sub>1</sub>) or ν(S-O). UV/Visible was all consistent with the TriPASC structure. Electronic absorption at 442 nm, corresponding to 1a<sub>2</sub>→9e (ε = 254 M<sup>-1</sup> cm<sup>-1</sup>); 362 nm to 8e→9e (ε = 878 M<sup>-1</sup> cm<sup>-1</sup>) and 276 nm to 12a<sub>1</sub>→9e (ε = 1343 M<sup>-1</sup> cm<sup>-1</sup>).

**Tributylammonium sulfatotrioxochromate (TriBASC) [N(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>H]<sub>2</sub>CrO<sub>3</sub>SO<sub>4</sub>:** C<sub>24</sub>H<sub>56</sub>N<sub>2</sub>O<sub>7</sub>SCr: Calcd. (%) C, 50.70; H, 9.859; N, 4.929. Found (%) C, 52.13; H, 10.21; N, 5.12. IR. (KBr, cm<sup>-1</sup>): 896 ν<sub>1</sub>(A<sub>1</sub>) or ν(CrO<sub>3</sub>), 973 ν<sub>4</sub>(E) or ν(CrO<sub>3</sub>) 1147 ν<sub>2</sub>(A<sub>1</sub>) or ν(S-O). UV/Visible was all consistent with the TriBASC structure. Electronic absorption at 442 nm, corresponding to 1a<sub>2</sub>→9e (ε = 232 M<sup>-1</sup> cm<sup>-1</sup>); 362 nm to 8e→9e (ε = 793 M<sup>-1</sup> cm<sup>-1</sup>) and 282 nm to 12a<sub>1</sub>→9e (ε = 1247 M<sup>-1</sup> cm<sup>-1</sup>).

**Oxidation of alcohols:** To a stirred solution of each alcohol in CH<sub>2</sub>Cl<sub>2</sub>, trialkylammonium sulfatotrioxochromate are added in one portion, at room temperature. The progresses of the reactions are monitored by TLC and UV/Visible spectrophotometry (at 354 nm). The mixture were stirred and refluxed for the time indicated in the Table-1 at room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub> and filtered. Evaporation of solvent furnished the product. The molar ratios of substrate to oxidants were 2:1. The solution became homogeneous briefly before the black-brown reduced reagent precipitated. Products are characterized by comparison with authentic samples (NMR, IR, TLC and m.p./b.p. measurement).

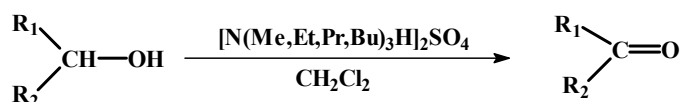
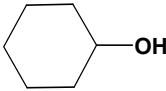
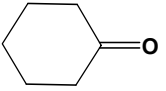
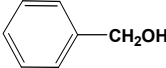
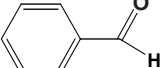


TABLE-1  
OXIDATION OF ALCOHOLS WITH TriRASC

	Substrate	Product	Time (min)	Yield (%)			
				TriMASC	TriEASC	TriPASC	TriBASC
1	<i>n</i> -C <sub>3</sub> H <sub>7</sub> -OH	<i>n</i> -C <sub>2</sub> H <sub>5</sub> -CHO	60	26	48	40	49
2	2-C <sub>3</sub> H <sub>7</sub> -OH	2-C <sub>2</sub> H <sub>5</sub> -CHO	60	22	23	30	30
3	<i>n</i> -C <sub>4</sub> H <sub>9</sub> -OH	<i>n</i> -C <sub>3</sub> H <sub>7</sub> -CHO	60	5	14	27	20
4	2-C <sub>4</sub> H <sub>9</sub> -OH	2-C <sub>3</sub> H <sub>7</sub> -CHO	60	31	12	34	3
5	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -OH	<i>n</i> -C <sub>4</sub> H <sub>9</sub> -CHO	60	14	25	10	27
6	<i>n</i> -C <sub>8</sub> H <sub>17</sub> -OH	<i>n</i> -C <sub>7</sub> H <sub>15</sub> -CHO	60	33	28	43	38
7			60	29	25	41	38
8			60	51	79	68	66

## RESULTS AND DISCUSSION

Trialkylammonium sulfatotrioxochromates could be easily prepared in good yield, quite stable when stored dry and in the absence of light and are active as oxidizing agents for the conversion of alcohols to carbonyl compounds.

$[\text{N}(\text{R})_3\text{H}]_2\text{CrO}_3\text{SO}_4$  were prepared by the reaction of relative triamine with  $\text{CrO}_3$  in 2:1 ratio and sufficient sulfuric acid in the water solvent.

There have been found that these reagents have certain advantages over similar oxidizing agents in terms of the amounts of oxidants and solvent required and especially in the short reaction times required and in the higher yields of the product (Table-1). The nature of the solvent does not appear to be particularly critical. Hydrocarbons, benzene, ethers and chlorinated hydrocarbons are equally effective, the practical choice being oriented by the solubility of the products and the desired reaction temperature. The IR spectra of TriRASC are similar to that of other sulfoxochromates<sup>28</sup>.

In conclusion, the quick preparation of these reagents, their stability, non-hygroscopicity, the ease of the work up of the reaction mixtures, reasonable yields of products and reaction time make trialkylammonium sulfatotrioxochromates versatile and practical reagents for the oxidation of alcohols and useful additions to the presently available bench reagents in organic synthesis. TriRASC reagents are easy to handle, could be weighed and have no hazardous effects.

During the reactions, the colour of the oxidant change from orange to colourful, providing visual means for ascertaining the progress of the oxidations. The results obtained with trialkylammonium sulfatotrioxochromates are quite satisfactory and show the new reagents as valuable addition to the existing oxidizing agents.

### ACKNOWLEDGEMENTS

The authors would like to thank Dr. Gh. Rezaei Behbahani and Dr. Mahjoub for valuable discussions.

### REFERENCES

1. G. Maier, H.P. Reisenauer and M.D. Marco, *Angew. Chem. Int. Ed.*, **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. Czech. Chem. Commun.*, **66**, 877 (2001).
4. M.M. Heravi, R. Kiakoojori, M. Mirza-Aghayan, K. Tabar-Hydar and M. Bolourtchian, *Monatsh. Chem.*, **130**, 481 (1999).
5. M.N. Bhattacharjee, M.K. Chaudhuri, H.S. Dasgupta and N. Roy, *Synthesis*, 588 (1982).
6. G.S. Chaubey, S. Das and M.K. Mahanti, *Croat. Chim. Acta*, **76**, 287 (2003).
7. F. Shirini, I. Mohammadpoor-Baltork, Z. Hejazi and P. Heravi, *Bull. Korean Chem. Soc.*, **24**, 517 (2003).
8. G.F. Jeyanthi, G. Vijayakumar and K.P. Elango, *J. Serb. Chem. Soc.*, **67**, 803 (2002).
9. R. Srinivasan, P. Stanley and K. Balasubramanian, *Synth. Commun.*, **27**, 2057 (1997).
10. A.R. Mahjoub, S. Ghammami and M.Z. Kassae, *Tetrahedron Lett.*, **44**, 4555 (2003).
11. J.C. Collins, W.W. Hess and F.J. Frank, *Tetrahedron Lett.*, **9**, 3363 (1968).
12. E.J. Corey and G.W.J. Fleet, *Tetrahedron Lett.*, **14**, 4499 (1973).
13. E.J. Corey and J.W. Suggs, *Tetrahedron Lett.*, **16**, 2647 (1975).
14. E.J. Corey and G. Schmidt, *Tetrahedron Lett.*, **20**, 399 (1979).
15. F.S. Guziec and F.A. Luzzio, *Synthesis*, 691 (1980).
16. M.N. Bahttcharjee, M.K. Chauduri, H.S. Dasgupta, N. Roy, K. Nrmalendu and T. Darlando, *Synthesis*, 7 (1982).
17. M.N. Bahttcharjee, M.K. Chauduri and S. Purkayastha, *Tetrahedron*, **43**, 5389 (1987).
18. M.N. Bhattacharjee and M.K. Chaudhuri, *Inorg. Synth.*, **27**, 310 (1990).
19. J. Drabowicz, *Synthesis*, 125 (1980).
20. V. Murugesan and A. Pandurangan, *Indian J. Chem.*, **31B**, 377 (1992).
21. R. Srinivasan, C.V. Ramesh, W. Madhulatha and K. Balasubramanian, *Indian J. Chem.*, **35B**, 480 (1996).
22. U. Bora, M.K. Chaudhuri, D. Dey, D. Kalita, W. Kharmawphlang and G.C. Mandal, *Tetrahedron*, **57**, 2445 (2001).
23. Y. Martinez, M.A. delas Heras, J.J. Vaquero, J.L. Garcianavio and J. Alvarezbuilla, *Tetrahedron Lett.*, **31**, 8513 (1995).
24. S. Ghammamy, H. Eimanieh and M.K. Mohammadi, *Synth. Commun.*, **37**, 601 (2007).
25. M.Z. Kassae, M. Hattami, A.R. Mahjoub and S. Ghammami, The Third Congress of Chemistry of Islamic Azad University, A-10 (2002).
26. S. Agarwal, H.P. Tiwari and J.P. Sharma, *Tetrahedron*, **46**, 4417 (1990).
27. Y.S. Cheng, W.L. Liu and S.H. Chen, *Synthesis*, 223 (1980).
28. K. Nakamoto, in: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons: New York, edn. 3, Vol. 1, pp. 140-150 (1978).