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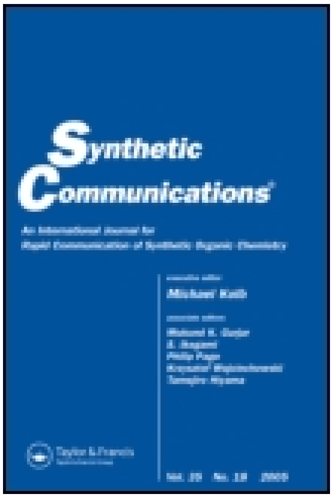

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Cetyltrimethylammonium Dichromate: A Phase-Transferring Oxidant

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Cetyltrimethylammonium Dichromate: A Phase-Transferring Oxidant

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Abstract: A phase-transferring oxidant, cetyltrimethylammonium dichromate (CTADC) has been prepared and characterized from elemental analysis and spectral data. Application of this reagent to oxidize alcohols, aldehyde, and cinnamic acid is reported.

Keywords: Cetyltrimethylammonium dichromate, phase-transferring agent, oxidation

In continuation of our search for novel oxidizing agents suitable for substrates in organic solvents, we have made an attempt to synthesize and establish cetyltrimethylammonium dichromate as a phase-transferring agent. Cetyltrimethylammonium (CTA) ion is well known for its amphipathicity, that is, having the characteristics of being solubilized in both aqueous and non-aqueous media. Unlike other quaternary ammonium ions (tetra butyl or octyl ammonium ions), CTA has a relatively small head group with more exposed charge and a well-balanced hydrophobic group to carry the ion to both water and organic media. Onium with its counterion forms a tight ion pair in organic solvents, whereas in aqueous medium it dissociates.[1] CTA with bromide as the counterion can form micelle in aqueous medium and can form reversed micelle in chloroform.

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Previously we reported the oxidation kinetics using cetyltrimethylammonium permanganate (CTAP)[2] on styrylpyridinium dyes,[3] substituted cinnamates[4] and cis-olefinic double bonds.[5] We have also synthesised cetyltrimethylammonium ceric nitrate (CTACe) and reported the oxidation behavior of this oxidant toward several organic substrates.[6] CTAP and CTACe can react effectively on organic substrates without any acid catalyst.

Oxidative applications of chromium(VI) range from oxidation of methylene group to carboxylic acids, which yields corresponding oxidized products. To carry Cr(VI) to organic solvents a variety organic carriers have been used. Onium ions are found to be highly successful as carriers of these counter ion.[7–15] Similar to normal ion exchangers, cetyltrimethyl ammonium ions can easily trap dichromate ions to form cetyltrimethylammonium dichromate (CTADC, **1**). The elemental analysis clearly envisages the presence of two CTA units per molecule of dichromate. The IR and NMR spectral data also supports the presence of CTA in the oxidant. The IR band at $933\,\mathrm{cm}^{-1}$ is evidence of the presence of a Cr-O group in the molecule.[16] Similarly, the chemical shift values around 3.42 and 3.51 δ, because of the onium methylene groups also support a closeness of the dichromate anion to the onium ion. In cetyltrimethylammonium bromide and cetyltrimethylammonium ceric nitrate these values appear at around 4.1 and 3.8 δ, respectively.[6]

$$[C_{16}H_{33}N^{+}(CH_3)_3]_2Cr_2O_7^{=}$$

1

CTADC is found to be water insoluble and soluble in most of the organic solvents. The Cr(VI) band ranges from 353 in dioxane to 383 in dichloromethane. CTADC is found to be stable in these solvents at reflux temperature and for an appreciable time period (24 h). Cetyl trimethyl permanganate has been reported to be unstable in solution and it is found to oxidize the CTA ion to corresponding pentadecanal.[2] In the present experimental conditions the substrates were refluxed with the oxidant in dicholoromethane for 0.5 to 6 h and the products were isolated by the solvent-extraction method from the reaction mixture. The products were identified by comparing the IR spectral data and melting/boiling points of the products or their derivatives. The experimental conditions and analytical data of the products are given in Table 1.

EXPERIMENTAL

General

Melting point and boiling (Siwoloboff's method)[17] points of the oxidation products and the 2,4-dinitro phenyl hydrazones were measured in an acid

Table 1. Reaction condition and product analysis of the oxidation reactions using CTADC

Substrate	Product	Reflux time (h)	Yield (%)	Melting/boiling point (°C, literature value)[17]	Melting point of 2,4-DNPH (literature value)[17]
Benzyl alcohol	Benzaldehyde	4.0	100	178–180,l (179)	237 (237)
p-Nitrobenzyl alcohol	*p*-Nitrobenzaldehyde	6.0	95	106,s (106)	—
Cyclohexanol	Cyclohexanone	3.0	90	154–157,l (156)	163 (162)
Benzoin	Benzil	3.0	100	93–95,s (95)	189 (189)
1-Octanol	1-Octanal	2.5	80	168–170,l (170)	105 (106)
Iso-propanol	Acetone	0.5	100	54–56,l (56)	128 (128)
p-Hydroxyquinone	*p*-Benzoquinone	0.5	100	115–117,s (116)	—
Benzaldehyde	Benzoic acid	1.0	100	121,s (121)	—
o-Chlorobenzaldehyde	*o*-Chlorobenzoic acid	4.0	90	140–141,s (141)	—
o-Methylbenzaldehyde	*o*-Methylbenzoic acid	4.0	85	104–105,s (105)	—
o-Methoxybenzaldehyde	*o*-Methoxybenzoic acid	4.0	80	99–101,s (101)	—
Cinnamic acid	Benzoic acid	3.5	90	121,s (121)	—

bath and are uncorrected. The 2,4-dinitrophenyl hydrazones of aldehydes were prepared by the standard method.[18] The IR spectra of the products and the 2,4-dinitrophenyl hydrazones were recorded on a Perkin Elmer RX-1 FTIR spectrometer in KBr disc. The solvents for absorption spectra measurements were purified by using the standard method[19] and distilled just before use. The absorption spectra were recorded on a Perkin Elmer Lambda EZ-201 UV-Vis spectrophotometer.

Synthesis of Cetyltrimethylammonium Dichromate

Potassium dichromate (2.94 g, 10.0 mmol) in water (100 ml) was added slowly to a stirred solution of cetyltrimethylammonium bromide (7.38 g, 20.0 mmol) in water (100 ml) at room temperature. After 15 min the yellow product was filtered and washed with water until no Br^- and dichromate were detected, which gave cetyltrimethylammonium dichromate (7.68 g, 98%), Mp 212°C. Analysis: C, 58.14; H, 10.65; N, 3.54; Cr, 13.11%. $C_{38}H_{84}O_7N_2Cr_2$ requires, C, 58.16; H, 10.71; N, 3.57; Cr, 13.26%. IR (in cm^{-1}): 771, 879, 933, 1467, 2850, 2921, 3028, 3471. NMR (δ) 0.86 (t, 6H), 1.29 (m, 48H), 1.67 (m, 4H) 1.74 (m, 4H), 3.42 (s, 18H), 3.51 (m, 4H).

General Method for Oxidation of Organic Substrate Using CTADC

The organic substrate (0.01 M) was refluxed with CTADC (2.66 g, 3.4 mmol) in chloroform (20 ml) and the reaction was monitored by spectrophotometer at 590 nm for Cr(111) in a chloroform solution. No further increase in the optical density indicated the completion of the reaction. The reaction mixture was concentrated and extracted with ether. Evaporation of ether gave the desired product.

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