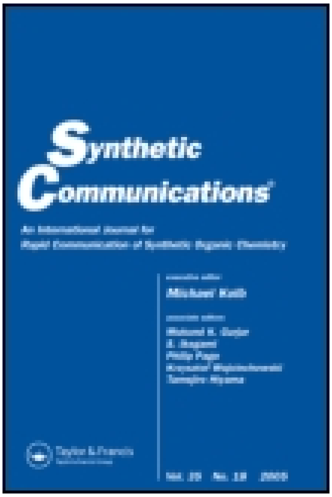

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Tetramethylethylenediammonium Bichromate (TMEDADC): A New Selective Oxidation Reagent

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TETRAMETHYLETHYLENEDIAMMONIUM DICHROMATE (TMEDADC): A NEW SELECTIVE OXIDATION REAGENT

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TMEDADC obtained from Chromium trioxide and TMEDA has been conveniently utilized for the selective oxidation of benzylic and allylic alcohols in excellent yield for the first time.

Chromium(VI) reagents in combination with amines have been widely used for the oxidation of alcohols to carbonyl compounds[1] and these reagents can be broadly classified into chlorochromate[2] series and dicromate[3] series based on the hydrochloric acid additive in the reagent preparation. It has been suggested beyond doubt that the nature of the amine determines the oxidizing property of the chromate ion and this is inversely related to the donor strength of the associated amine ligand[4]. Majority of the chlorochromate and dichromate series of reagents oxidise alcohols to corresponding carbonyl compounds without discrepancy. Exceptions are N,N-dimethylamino pyridinium chlorochromate (DMAPCC)[5], Benzyl triethyl ammonium chlorochromate[6]

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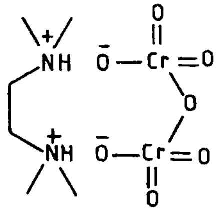
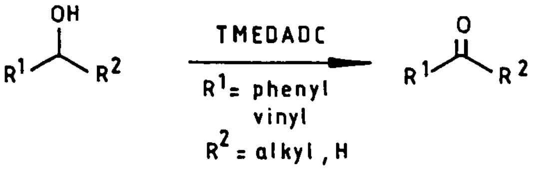
and Pyridinium chlorochromate in combination with crown ethers[7] which are selective and oxidise only benzylic and allylic alcohols. However, these reagents have hydrochloric acid additive and also the reagents preparation involve expensive amine partner and/ or phase transfer catalysts. Keeping some of these limitations in mind we have prepared a new, stable dichromate reagent TMEDAC(1) for the first time, which is very mild and selective in oxidation. The details are documented herein (equation 1).



1

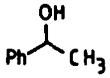
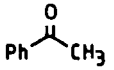
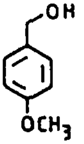
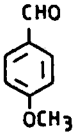
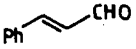
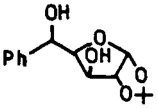
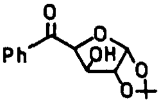
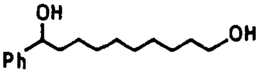
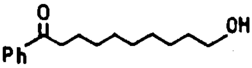
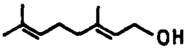
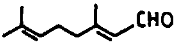
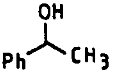
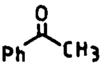
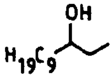
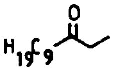
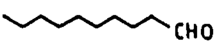
The reagent is conveniently prepared analogues to pyridinium dichromate[8] except that amine partner has two tertiary amine groups which makes this new reagent more basic than other existing dichromate reagents. This increased basicity makes the reagent less active and thus more selective (*vide infra*).



eq.1

To establish the efficacy and selectivity of the reagent under study, several alcohols were exposed to TMEDADC in methylene chloride at reflux (Table 1). As expected, only benzylic and allylic alcohols provided the corresponding carbonyl compounds in excellent yields (entries **1,2,3,7**), however less reactive primary (entry **9**) and secondary (entry **10**) alcohols were almost unaffected even after addition of excess of the reagent and prolonged reaction hours. This contrast in behaviour led us also to investigate the utility of TMEDADC in selective oxidation of diols wherein one of the hydroxy groups is allylic/benzylic whereas the other is a simple primary or secondary. In all the cases under examination (entries **4,5,6**) only the more reactive benzylic or allylic alcohol got oxidized and the other remained unaffected. Similarly

Table 1

Entry	Substrate	Product (yield %)[a]	Reaction time
1		 (90)	16 h
2		 (90)	12 h
3		 (90)	12 h
4		 (80)	8h
5		 (70)	12h
6		 (75)	12 h
7		 (67)	12h
8	 + 1-decanol	 + 1-decanol (85[b])	24h
9		 (5[c])	24h
10		 (5)	12 h

a) *Percentage yields based on the isolation of chromatographically homogeneous products.*

b) *No traces of 1-decanol oxidised product was observed.*

c) *Portionwise addition of the reagent over a long period (30 hours) resulted in 5-10% of oxidised product.*

when a mixture of 1-decanol and α-hydroxy ethylbenzene (entry **8**) was treated with 4 equivalents of TMEDADC only the α-hydroxy ethylbenzene got oxidized to acetophenone where as 1-decanol got unaffected. In summary it is pertinent to mention that a new selective oxidizing reagent has been developed which is economical compared to most of the existing chromium reagents and also MnO_2[9] (which is required in large excess) for a similar functional group transformation.

Preparation of Tetramethylethylenediammonium dichromate (TMEDADC)[10]:

To chromium(VI) oxide (10g; 0.1 mole) in 10ml of H_2O at -15°C(ice/salt) was added TMEDA(15ml) and stirred for 1h. The bright orange solid formed was diluted with 25ml acetone and filtered and washed with 2x10ml acetone (yield 20g; 86%). m.p.153°C. ^{1}H NMR (D_2O, 200MHz) : 3.80 (S, 4H); 3.11 (S, 12H); IR (KBr, cm^{-1}) 930, 875, 765, 730 (characteristics of dichromate ion)[11].

Oxidation of alcohols with TMEDADC. General Procedure :

A mixture of the alcohol (2 mmoles) and TMEDADC (6 mmoles) in CH_2Cl_2 (10ml) is refluxed for the completion of reaction (8-12h), cooled, filtered through a pad of celite or silicagel to furnish the carbonyl compound (for yield see Table 1).

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