Tetradecyltrimethylammonium permanganate: a novel potassium permanganate derived reagent for trans-dichlorination, trans-dibromination and cis-dihydroxylation of olefins

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Reactivity of KMnO₄ has been modified by converting it into long chain quaternary ammonium permanganate salt, viz., tetradecyltrimethylammonium permanganate (TDTAP). This new versatile, stable reagent has been utilised for chemoselective and stereoselective trans-dichlorination and dibromination of a variety of alkenes. Use of this reagent for vicinal dihydroxylation of alkenes in a two phase solvent system has also been demonstrated. The mechanism for the trans-dichlorination reaction and the nature of the reacting species has been proposed.

Potassium permanganate exhibits unique reactivity towards olefins. However its utility in organic synthesis has been severely limited by solubility problems. In an attempt to improve and modify the reactivity of potassium permanganate, several quaternary ammonium permanganates have been prepared, characterised and used. Solubility studies indicate that these compounds exist in solution as either ion pair or aggregates, with aggregation being promoted by high concentration, low temperature and solvents of low polarity. Detonation of quaternary ammonium permanganates during drying at elevated temperatures have been reported.

A systematic study has shown that salts containing unsaturated groups in the cation (PhCH₂N⁺Et³, PhCH₂N⁺Me³, Ph₃N⁺Me, C₅H₅N⁺Me) decomposed with explosive violence when the temperature is reached 80–90°. Compounds with a saturated alkyl chain (Et₄N⁺, Bu₄N⁺, CH₃(CH₂)₁₅N⁺Me³), on the other hand, showed no explosive tendency, but they did decompose passively between 80° and 100°.

We have recently prepared tetradecyltrimethylammonium permanganate (TDTAP) salt and demonstrated its use as an excellent reagent for the chemoselective and stereoselective trans-dichlorination and dibromination of a variety of alkenes. Vicinal dihydroxylation of alkenes with TDTAP and potassium hydroxide in a two phase solvent system has also been reported by us.

TDTAP, a violet crystalline solid, stable at room temperature for a few days, can be stored at 0° in a brown bottle for months and is highly soluble in methylene dichloride.

This new reagent is readily prepared as follows:

\[ C_{14}H_{29}N⁺Me₃Br⁻ + K⁺MnO₄ \rightarrow \]
\[ \text{Aqueous solution} \rightarrow \text{Aqueous solution} \]
\[ C_{14}H_{29}N⁺Me₃MnO₄ \]
\[ \text{Violet crystalline solid} \]

To a stirred solution of potassium permanganate (7.9 g, 50 mmol) in water (250 ml) at 25° was added dropwise over 30 min a solution of tetradecyltrimethylammonium bromide (17.5 g, 52 mmol) in water (250 ml) when a violet coloured precipitate formed immediately. The mixture was stirred for further 30 min the violet precipitate was filtered off, washed thoroughly with water and dried in vacuo over P₂O₅ to furnish TDTAP (17.25 g, 92%), m.p. 165–170°.

The main disadvantage of the related reagent benzyltrimethylammonium permanganate is its instability, arises because of the easily formed benzyl radical initiates a chain reaction during drying or when this reagent is handled neat. In view of this it was expected that replacement of benzyl group by a long chain hydrocarbon radical, e.g. tetradecyl, would give rise to increased stability and solubility.

Differential thermal analysis of TDTAP has shown its decomposition to be stepwise exothermic process which starts at 102.3°, with the thermogram reaching a maxima at 119.5°. This clearly indicates that TDTAP decomposes passively at a relative higher temperature compared with earlier reported quaternary permanganate salts. In fact, as mentioned earlier, this salt being stable for months at 0° permits its ready access, whenever required.

* Dedicated to Professor S. M. Mukherji.
Manganese-mediated stereoselective and chemoselective trans-dichlorination of alkenes with tetradecyltrimethylammonium permanganate-trimethylchlorosilane

Formation of vic-dichlorides by addition of molecular chlorine to olefins has limited synthetic utility due to the occurrence of side reactions. Moreover, use of gaseous chlorine presents a potential environmental hazard and its quantitative utilization is hard to work out. Several other reagents add chlorine to double bonds. Sulfuryl chloride reacts readily with most of the ethylenic compounds to yield saturated dichloro derivatives with evolution of sulfur dioxide. Reaction of trichloroamine with olefins provides a simple means for the preparation of vic-dichlorides. Phosphorous pentachloride, antimony pentachloride, iodobenzene dichloride, tetrabutylammonium iodotetra-chloride and copper(II) chloride have been examined as chlorinating agents with good results in certain cases. cis-Vicinal dichlorinations of olefins by molybdenum(VI)-acetyl chloride and manganese(III) acetate-calcium chloride have been reported. trans-Vicinal dichlorination of olefins with manganese dioxide-trimethylchlorosilane and MnO2·MnCl2·acetyl chloride have been documented. However, non-homogeneity of these inorganic based reagents in commonly used organic solvents limits their wider synthetic applications. In order to overcome this difficulty Marco et al. used benzyltriethylammonium perrnanganate and oxalyl chloride in methylene dichloride. Recently these authors also reported the use of KMnO4-trimethyl-chlorosilane in the presence of benzyltriethylammonium permanganate and oxalyl chloride in methylene dichloride. The reaction of 16-dehydropregnenolone acetate and carvone in methylene dichloride with excess of chlorine gas at 0 to 30°C for 1.5 h furnished a complex reaction mixture of polychlorinated products. Addition of chlorine to both double bonds took place in both the cases. Column chromatographic purification of polychlorinated products afforded 3,5-acetoxy-5,6,17-tetrachloro-5α-pregnan-20-one, 3β-acetoxy-5,6,16,17-tetrachloro-5α-pregnan-20-one from 16-DPA and two more unidentified compounds. The desired 5,6-dichlorinated product could not be isolated from this reaction. In case of carvone also hepta and nona chlorinated products were isolated by column chromatography. No trace of the desired 9,10-dichlorocarvone was found in this chlorination reaction. On the other

| Starting compound | Product | Yield (%) |
|-------------------|---------|-----------|
| 16-DPA 3          | 9       | 96        |
| Carvone 5         | 10      | 88        |
| 16-DPA 3          | 11      | 87        |
| Benzyltriethylammonium permanganate 6 | 12      | 92        |
| Antimony pentachloride 10 | 13      | 62        |
| Iodobenzene dichloride 11 | 14      | 84        |
| Tetrabutylammonium iodotetra-chloride 12 | 15      | 90        |
| Copper(II) chloride 13 | 8       | No Reaction |
hand treatment of compounds 16-DPA 3 and carvone 5 with excess of TDTAP-TMCS in methylene dichloride under identical conditions led to the desired dichlorides 11 and 13 as the only products in high yield comparable with those obtained when a single equivalent of TDTAP had employed. This excellent chemoselectivity clearly ruled out the possibility of generation of molecular chlorine in the reaction mixture and strongly suggest the formation of an oxochloro manganese intermediate as a chlorinating species.

A violet-coloured solution of TDTAP in methylene dichloride at 0 to 3° changed immediately to brown on treatment with TMCS. A solution of olefin in methylene dichloride was added to this mixture which was then stirred at 0 to 3° for 1.5 h. During this period the reaction mixture turned green. Along with trans-dichlorinated products, we isolated hexamethyldisiloxane as one of the end products in this reaction.

In order to identify the nature of the actual reacting species in the trans-dichlorination reaction, we have carried out UV-visible absorption and EPR spectroscopic studies of the starting violet coloured solution of TDTAP in methylene dichloride, the brown intermediate (reacting species) formed after addition of TMCS and the final green coloured methylene dichloride solution. The UV-visible spectrum of the starting homogeneous violet coloured solution of TDTAP in methylene dichloride showed similar pattern as that of a solution of KMnO₄ in methylene dichloride and acetonitrile mixture.

EPR spectrum of solution of TDTAP in methylene dichloride, shows a straight line (EPR inactive). This confirms the (+VII) oxidation state of manganese in quaternary ammonium permanganate salt with no unpaired electrons.

The UV-visible spectrum of the intermediate brown species formed by addition of trimethylchlorosilane to the violet coloured solution of TDTAP in methylene dichloride at 0° showed a hypsochromic shift having new maxima at 400 nm with complete disappearance of the permanganate band centered at 526 nm. This intermediate brown species furnished a sharp six line EPR spectrum which clearly indicates the presence of lower valent manganese species with unpaired electrons.

The UV-visible spectrum of the green colored solution formed after completion of the dichlorination reaction showed a bathochromic shift with a new maxima at 414 nm. The EPR spectrum of this final green coloured solution showed altogether different splitting pattern with hyperfine lines.

All these spectral data suggest that Mn (VII) in TDTAP is reduced by addition of TMCS to a lower valent Mn-chlorine species. This species in turn delivers two chlorine atoms in a stereoselective manner to the olefin and thus furnishing the trans-dichlorinated product. There is a two step change in the oxidation state of permanganate in the course of the reaction. The preparation and spectral properties of some of the oxochlorides of manganese are reported. Among these oxochlorides, manganese oxide trichloride (MnCl₃) showed UV-visible maxima at 400 nm. Similar UV-visible absorption at 400 nm has been recorded for the brown species generated by the addition of TMCS to violet coloured solution of TDTAP in methylene dichloride. We failed to isolate any of the dichlorinated products when the chlorination reaction was carried out at a temperature higher than 5°. The brown species seems to be unstable and slowly (10 minutes) turns to green above 5° and immediately turns green on addition of TMCS to TDTAP solution at 25°.

The close resemblance of UV-visible spectrum and stability pattern of the brown species with that of MnOCl₃ leads us to propose the formation of MnOCl₃ in the reaction medium, which inserts two chlorine atoms in a stepwise manner to the alkene (Scheme I).

Manganese-mediated novel trans-dibromination of olefins with tetradeyltrimethylammonium permanganate and trimethylbromosilane

Olefins are usually treated with molecular bromine in solvents such as carbon tetrachloride, chloroform, carbon disulfide, acetic acid, ether or ethyl acetate to form dibromides. For small scale preparations pyridinium bro- mide perbromide is the reagent of choice. Copper(II) bromide also react with olefins in the presence of acetonitrile, methanol or triphenyl phosphate to furnish exclusively vicinal dibromoalkanes in high yields. Anion exchange resins act as a bromine carrier and hydrobromic acid, hydrogen
peroxide and benzyltrimethylammonium chloride in carbon tetrachloride have been used\textsuperscript{28} to brominate alkenes. TDTAP in combination with trimethylbromosilane (TMBS) provides\textsuperscript{4} a simple and mild method for stereoselective and chemoselective \textit{trans}-dibromination of alkenes (Table 2).

| Starting compound | Product | Yield (%) |
|-------------------|---------|-----------|
| 1                 | ![Image](1) | 91        |
| 2                 | ![Image](2) | 85        |
| 3                 | ![Image](3) | 89        |
| 4                 | ![Image](4) | 79        |
| 5                 | ![Image](5) | 73        |
| 7                 | ![Image](7) | 62        |
| 16                | ![Image](16) | 60        |
| 17                | ![Image](17) | 60        |
| 18                | ![Image](18) | 91        |
| 19                | ![Image](19) | 85        |
| 20                | ![Image](20) | 89        |
| 21                | ![Image](21) | 79        |
| 22                | ![Image](22) | 73        |
| 23                | ![Image](23) | 62        |
| 24                | ![Image](24) | 60        |
| 25                | ![Image](25) | 60        |

Table 2. \textit{trans}-Dibromination of alkenes with TDTAP-TMBS

A violet-coloured solution of TDTAP in methylene dichloride at 0 to 3° changed immediately to deep brown on treatment with TMBS. The olefin in methylene dichloride was added to this mixture which was then stirred at 0 to 3° for 1.5 h.

This TDTAP-TMBS reagent displays high chemoselectivity as evidenced by no reaction of \(\alpha,\beta\)-unsaturated double bond at C-16 of 16-dehydropregnenolone acetate 3, the electron-deficient double bond of carvone 5 and nona-3,8-dien-2-one 17. In the stigmasterol derivative 2,22-dien-6-one 2 the 22-\(E\)-double bond is sterically hindered by the (24S)-ethyl and D ring of the steroid, thus hindering the approach of the brominating species. The only product isolated in this case is 2,3-diaxial dibromide 19.

The probable pathway for the \textit{trans}-vicinal dibromination of alkenes with TDTAP-TMBS can be represented as follows (Scheme 2).

\[ \text{[N(Me)C_6H_4][MnO_2]} + 2 \text{Me_3SiBr} \]

\[ \begin{array}{c}
\text{Br} \\
\text{Br}
\end{array} + \text{Me_3Si-O-SiMe}_3 \]

A similar complex mixture formed containing small amount of same dibromide. With TDTAP-TMBS formation of dibrominated compound 19 as a single product in very good yield strongly suggests that \textit{trans}-dibromination occurs by a different pathway and clearly rules out the possibility of generation of molecular bromine in the reaction medium as the brominating species.

Vicinal dihydroxylation of alkenes with tetradecyltrimethylammonium permanganate and potassium hydroxide in a two-phase solvent system

Potassium permanganate is a very strong oxidizing agent. It has been established beyond doubt that the low-temperature oxidation of alkenes with aqueous alkaline potassium permanganate yields mainly 1,2-glycols, by \textit{cis}-dihydroxylation. The cyclic manganese(\(V\)) ester intermediate is unstable, and is rapidly hydrolysed at both C-O-Mn bonds, more or less simultaneously to yield diols\textsuperscript{29-31}. The yields of diols, however are seldom above 50% though they can be improved with phase transfer catalysis\textsuperscript{32-34} or increased.
Preparation and absorption spectrum of a stable solution of manganese(V) diester by reacting alkenes with pulverised potassium permanganate in dichloromethane and benzyltrimethylammonium chloride as a phase transfer agent has been reported by Ogino and his group. It is probable that the intermediate manganate(V) diester could be more stable under these conditions because it would be complexed with the quaternary ammonium ion and the hydrolysis reaction would be suppressed in the absence of water. This procedure provided a simple route to a number of dialdehydes from alkenes in good yields. The first example of the use of stable cetyltrimethylammonium permanganate salt for the cis-dihydroxylation of alkenes has been published by Chandrasekaran and co-workers.

As an extension of Chandrasekaran's work and to some extent Ogino's work, we have reported the first practical and acceptable yields of vicinal cis-diols from alkenes with tetradecyltrimethylammonium permanganate (TDTAP) salt and addition of potassium hydroxide at the beginning in tert-BuOH-CH₂Cl₂-H₂O as the solvent system.

Treatment of alkene (1 mmol) in CH₂Cl₂ with solution of TDTAP (1.2 mmol) in CH₂Cl₂ for 2 h at 30° followed by anhydrous or alkaline work-up (Method A), the yields of diol from the alkenes we used are poor to moderate (Table 3). Carrying out the reaction in aqueous tert-butanol followed by treatment with alkali even lowers the yield of the diols. Continuing the reaction for a longer period does not improve the yield of diols. In all the cases varying amounts of starting materials recovered unchanged.

We found that when the reaction was conducted in a two phase solvent system of tert-butanol, CH₂Cl₂ and water in the ratio 50 : 10 : 1.25 in the presence of 0.1 mmol of KOH (Method C), dihydroxylation occurs in good yield. In the beginning, the pH of the reaction mixture is 7.5, which changes to 9.5 after the addition of aqueous KOH and remains the same throughout the entire reaction. The beneficial effect of addition of alkali at the beginning on the yields of diols in KMnO₄ oxidation of olefins is well known. A delicate balance for the formation of intermediate cyclic manganese(V) ester, its life time and its instant hydrolysis in alkaline condition (present from the beginning) in a two phase solvent system account for the increased diol formation.

Using benzyltrimethylammonium hydroxide as a base at the beginning in non aqueous solvent system of tert-butanol and CH₂Cl₂ (Method B), reasonably good yields of the diols are realised (Entry 1–4 in Table 3). Here again the delicate balance of the formation of cyclic ester and its hydrolysis with base soluble in the organic medium are responsible for the formation of the diols in respectable yields. TDTAP is a reagent derived from potassium permanganate. It is very much expected that this reagent will add two -OH groups to a double bond like alkaline KMnO₄ or OsO₄ to give cis-diol from the less hindered side of the double bond. The exo, cis-diol is the product of selective oxidation of endo-dicyclopentadiene (Table 3). It is known that the non bornane double bond of dicyclopentadiene is the more reactive of the two. Again, the dihydroxylation of 16-dehydroprogesterone acetate takes place on the electron deficient α,β-unsaturated ketone to afford 3β-acetoxy-16α,17α-dihydroxyprogesterone-5-en-20-one. Potassium permanganate hydroxylation and continuous permanganate oxidation of 16-DPA, introduced the two cis-OH group at 16, 17 position from the less hindered side of the double bond.

Table 3. Dihydroxylation of alkenes with TDTAP

| Starting compound | Product | Method | Yield (%) |
|-------------------|---------|--------|-----------|
| A                 | 21      | B      | 51        |
| A                 | 29      | B      | 56        |
| A                 | 21      | B      | 50        |
| A                 | 45      | B      | 69        |
| A                 | 27      | B      | 47        |
| A                 | 44      | B      | 83        |
| A                 | 32      | B      | 75        |
| A                 | 39      | B      | 56        |
| A                 | 44      | B      | 62        |
bond to give same compound 32, leaving the 5,6-double bond unaffected.

cis-Diols were obtained in high yields from the corresponding alkenes using TDTAP, in a biphasic solvent system with inorganic base, or a homogenous system with organic base present from the beginning of the reaction.

General procedure: Method A: To a stirred solution of TDTAP (0.420 g, 1.12 mmol) in dichloromethane (10 ml) a solution of cholest-2-ene-6-one 1 (0.384 g, 1 mmol) in dichloromethane (12 ml) was added. The reaction mixture was stirred for 2 h at 30°. It was then treated with 5% aqueous NaOH (5 ml), stirred for 30 minutes. Usual work up followed by column chromatography over silica gel afforded pure cholest-2a,3a-diol-6-one 30 (0.088 g, 21%) and starting material (0.204 g, 69%) was recovered back. (Carrying out the reaction in aqueous tert-butanol followed by treatment with alkali gave even lower yield).

Method B: A solution of cholest-2-ene-6-one 1 (0.384 g, 1 mmol) in tert-BuOH (8 ml) and CH2Cl2 (4 ml) was added to benzyltrimethylammonium hydroxide (0.334 g, 2 mmol). To this magnetically stirred mixture, TDTAP (0.420 g, 1.12 mmol) was added in small portions during 2 min at 30°. The reaction mixture was stirred at this temperature for 1 h and then quenched with saturated aqueous solution of sodium bisulphite solution (10 ml). Usual work up followed by column chromatography over silica gel afforded pure cholest-2α,3α-diol-6-one 30 (0.213 g, 51%) and starting (0.047 g, 16%) was recovered back.

Method C: To a magnetically stirred solution of cholest-2-ene-6-one 1 (0.384 g, 1 mmol) in tert-BuOH (10 ml) and CH2Cl2 (2 ml) at 30° was added a solution of KOH (0.006 g, 0.1 mmol) in water (0.5 ml) followed by TDTAP (0.420 g, 1.12 mmol) in small portions during five min. The reaction mixture was stirred at this temperature for 1 h and then quenched with saturated aqueous solution of sodium bisulphite solution (10 ml). Usual work up followed by column chromatography over silica gel afforded pure cholest-2α,3α-diol-6-one 30 (0.305 g, 73%).

Conclusion: Reactivity of KMnO4 has been modified by converting it into long chain quaternary ammonium salt, tetracyclo[tridecyltrimethylammonium permanganate. This novel reagent has been utilised for chemoselective and stereoselective trans-dichlorination, dibromination and vicinal dihydroxylation of a variety of alkenes. The UV-visible spectrum, EPR studies and stability pattern of the reacting brown species with that of MnOCl3 lead us to propose the formation of MnOCl3 in the reaction medium, which inserts two chlorine atoms in a stepwise manner to the alkene. Formation of molecular chlorine in the reaction medium has been completely ruled out.

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