Manganese-mediated Novel Dibromination of Olefins with Tetradecyltrimethylammonium Permanganate and Trimethylbromosilane†

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The synthetic utility of tetradecyltrimethylammonium permanganate–trimethylbromosilane as an excellent new reagent for the stereo- and chemo-selective *trans*-dibromination of alkenes is reported.

Olefins are usually treated with a solution of bromine in carbon tetrachloride, chloroform, carbon disulfide, acetic acid, ether or ethyl acetate to form 1,2-dibromides,[1] although commercially available pyridinium bromide perbromide is convenient for the addition of bromine to a double bond on a small scale.[2] Copper(II) bromide also reacts readily with olefins in the presence of acetonitrile, methanol or triphenylphosphine to furnish[3] exclusively vicinal dibromoalkanes in high yields. Anion-exchange resins act as a bromine carrier[3] and hydrobromic acid, hydrogen peroxide and benzyltrimethylammonium chloride in carbon tetrachloride have been used[3] to brominate alkenes. Although there is no report of metal-mediated *trans*-dibromination of alkenes, *cis*-dichlorination[4] and *trans*-dichlorination[5] are known. Whilst potassium permanganate exhibits[6] unique reactivity towards olefins, its limited solubility has curtailed its use in organic synthesis. In an attempt to overcome this problem we have prepared tetradecyltrimethylammonium permanganate (TDTAP), a reagent which in combination with trimethylbromosilane (TMBS) provides a simple and mild method for stereo- and chemo-selective *trans*-dibromination of alkenes. *trans*-Vicinal dibromination with this reagent is reported here for the first time.

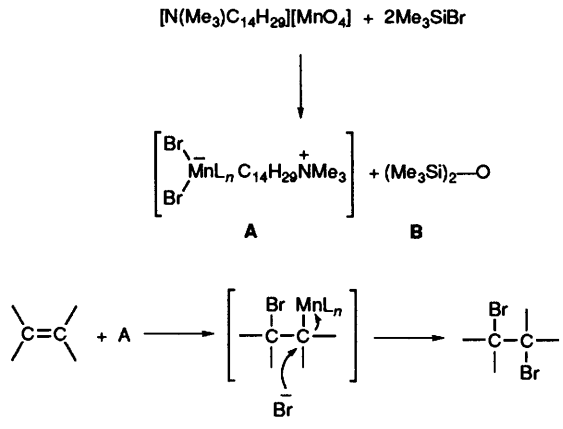
Results and Discussion

TDTAP, a violet crystalline solid stable at room temperature for a few days, can be stored at 0 °C in a brown bottle for months. This new reagent is readily prepared by mixing equimolar amounts of aqueous potassium permanganate and tetradecyltrimethylammonium bromide to give a violet precipitate which maybe filtered off. The main disadvantage of the related reagent[7] benzyltriethylammonium permanganate, its instability, arises because the easily formed benzyl radical initiates a chain reaction, during drying or when this reagent is handled neat; the reagent has also been reported[7] to detonate during drying. In view of this it was expected that replacement of the benzyl group by a long chain hydrocarbon radical, *e.g.* tetradecyl, would give rise to increased stability and solubility. This proved to be the case.

A violet-coloured solution of TDTAP in methylene dichloride at 0 to 3 °C changed immediately to deep brown on treatment with TMBS. The olefin in methylene dichloride was added to this mixture which was then stirred at 0–3 °C for 1.5 h. The results are summarised in Table 1.

This TDTAP–TMBS reagent displays high chemoselectivity as evidenced by no reaction of the α,β-unsaturated double bond at C-16 of pregnenolone acetate **3**, the electron-deficient double bond of carvone **4** and nona-3,8-dien-2-one **8**. In the stigmasterol derivative **1** the 22*E*-double bond is sterically crowded by the (24*S*)-ethyl and D ring of the steroid, thus hindering the approach of the brominating species. The only product isolated in this case is the 2,3-diaxial dibromide **9** (91%).

The probable pathway for the *trans*-vicinal dibromination of alkenes with TDTAP–TMBS can be represented as follows.



The observed colour change from violet of TDTAP in methylene dichloride to that of the dark brown brominating reagent can be rationalised in terms of formation of an intermediate manganese bromine species **A**. This species apparently inserts two bromine atoms in a stepwise manner giving, eventually, lower valent manganese; we have isolated hexamethyldisiloxane **B**. The reaction of pregnenolone acetate **3** in methylene dichloride at 0 to 3 °C with 1 mol equiv. of bromine in methylene dichloride is instantaneous. The product isolated after 3 min is the 5α,6β,16β,17α-tetrabromide (21%; m.p. 165–167 °C) starting pregnenolone acetate **3** (76%) with no trace of the 5α,6β-dibromide **11**. The stigmasterol derivative **1** on reaction with 1 mol equiv. of bromine in methylene dichloride at 0–3 °C for 5 min furnished a complex mixture of products from which a small amount of 2β,3α,22,23-tetrabromide (6%; m.p. 218–221 °C) was isolated. With 2 mol equiv. of bromine at 0–3 °C for 1.5 h a similar complex mixture formed containing a little of the same tetrabromide. With TDTAP–TMBS formation of the dibrominated compounds **11** and **9** as a single product and in good yield strongly suggests that *trans*-dibromination occurs by a different pathway and clearly ruling out the possibility of generation of molecular bromine in the reaction medium as the brominating species.

Experimental

Tetradecyltrimethylammonium Permanganate (TDTAP).—To a stirred solution of potassium permanganate (7.9 g, 50 mmol) in water (250 cm^3) at 25 °C was added dropwise over 30 min a solution of tetradecyltrimethylammonium bromide (17.5 g, 52 mmol) in water (250 cm^3). A violet coloured

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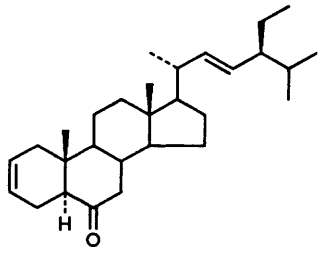
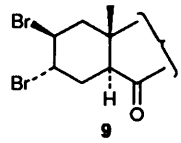
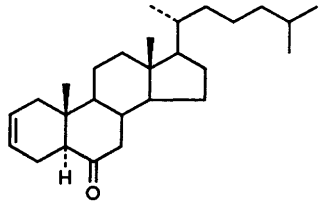
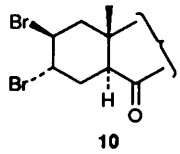
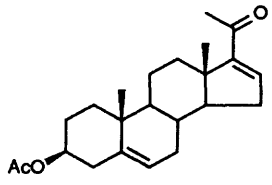
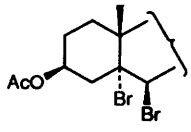
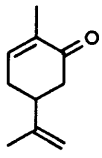
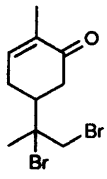
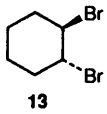
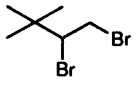
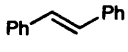
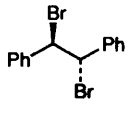
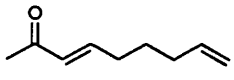
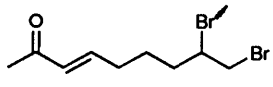
Table 1

Entry	Starting	Product	Yield(%)	M.p. (°C) [lit.] b.p. (°C)/Torr
1		 **9**	91	194–195
2		 **10**	85	134 [131[8]]
3		 **11**	89	119 [121[9]]
4		 **12**	73	65–70/0.3 Torr [40/0.04 Torr[10]]
5		 **13**	79	98/8 mm [101/ 14 Torr[11]]
6		 **14**	62	88–90/9 Torr [91–92/14 Torr[12]]
7		 **15**	60	235 [237[13]]
8		 **16**	60	125–130/0.075 Torr

precipitate formed immediately and the mixture was stirred for a further 30 min. The violet precipitate was filtered off, washed thoroughly with water (5 × 50 cm^3) and dried *in vacuo* over P_2O_5 to furnish the salt (17.25 g, 92%), m.p. 165–170 °C (decomp.); this was crystallised from CH_2Cl_2 (Found: C, 54.5; H, 10.3; N, 4.0. $C_{17}H_{38}NMnO_4$ requires C, 54.40; H, 10.13; N, 3.73%).

trans-*Bromination of Alkenes: a Typical Procedure.*—To a magnetically stirred violet-coloured solution of TDTAP (188 mg, 0.5 mmol) in methylene dichloride (10 cm^3) was added trimethylbromosilane (154 mg, 1.025 mmol) in methylene dichloride (2 cm^3) at 0–3 °C. A dark brown solution was formed immediately. To this (24*S*,22*E*)-ethyl-5α-cholestan-2,22-dien-6-one **1** (205 mg, 0.5 mmol) in methylene dichloride (2 cm^3) was added dropwise during 3 min. The reaction mixture was stirred at 0–3 °C for 1.5 h. After this it was stirred with 10% aqueous sodium bisulfite (10 cm^3) and then brought to room temperature. Methylene dichloride was removed from the colourless reaction mixture on a rotary evaporator after which the latter was extracted with ether (3 × 50 cm^3). The combined extracts were washed with water (2 × 30 cm^3) and brine (2 × 50 cm^3) and then evaporated under reduced pressure to afford (2*S*,3*S*,24*S*,22*E*)-2,3-dibromo-24-ethyl-5α-cholestan-22-en-6-one **9** (271 mg, 91%) as a solid. This was recrystallized from light petroleum (b.p. 60–80 °C)–methylene dichloride,

m.p. 194–195 °C (Found: C, 60.95; H, 8.1; $C_{29}H_{46}Br_2O$ requires C, 61.05; H, 8.07%); $[\alpha]_D^{30}$ +39.7* (*c* 0.99 in $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 (ketone); δ_H(200 MHz; $CDCl_3$) 0.7 (s, 3 H, 18-H_3), 0.82 (d, *J* 6† 6 H, 26, 27-H_3), 0.87 (t, *J* 7, 29-H_3), 1.04 (d, *J* 6, 21-H_3), 1.12 (s, 3 H, 19-H_3), 2.92 (dd, *J* 2, 12, 5-H), 4.7 and 4.9 (m, 2 H, 2, 3-H) and 5.12 (m, 2 H, 22, 23-H).

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* [α] Values expressed in units of 10^{-1} deg cm^2 g^{-1}.
† Values expressed in Hz.

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