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Trityl bromide was obtained from Aldrich and 6-iodo-1-heptene (**1**) was prepared from its tosylate and sodium iodide as reported earlier.[6]

5-Chloro-1-cyclooctene (**4**), 5-bromo-1-cyclooctene (**3**), and 5-iodo-1-cyclooctene (**2**) can be obtained in nearly quantitative yield by Pritzkow's method of adding dry HX to 1,5-cyclooctadiene in CH_2Cl_2.[13]

Gas chromatographic analyses were conducted on a Hewlett-Packard Model 700 instrument using a FID detector and packed columns. Quantitative GLC analyses were obtained with the use of response factor corrected peak areas using internal standards.

Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrophotometer.

Mass spectra were obtained on a Varian MAT 112S, and for EPR studies spectra were recorded on a Varian E 109 ES.

General Procedure for Reduction of Alkyl Halides. The appropriate amounts of alkyl halide (0.1 M) and metal hydride (0.2 M) were combined in a reaction tube under N_2 in THF and shielded from light. For the EPR study, the reagents were combined in an EPR tube under N_2. In those cases where DCPH or DCPD were employed, the additive was added to the metal hydride, followed by the addition of the appropriate alkyl halide. Control experiments showed that no reaction occurred between $LiEt_3BD$ and DCPH, as determined by the constancy of the P–H stretching band at 2260 cm^{-1} in THF at room temperature. DCPH was also unreactive (as determined by GLC) toward alkyl halides in the absence of $LiEt_3BH$.

At the chosen time, reaction mixtures were carefully quenched with water, internal standard added, and GLC analyses performed. A 20-ft column of 8% Apiezon L was used at 70 °C to separate the products formed in the reactions with benzene as internal standard. The iodides were analyzed by using a 4-ft column of 8% Apiezon L at 70 °C with *n*-decane as internal standard. The products were identified by comparing their retention times with the retention times of authentic samples.

Deuterium incorporation was evaluated by GC–mass spectroscopy.

Acknowledgment. We are indebted to the National Science Foundation Grant No. CHEM 78-00757 for support of this work.

Registry No. 1, 13389-36-1; **2**, 32654-09-4; DCPD, 91523-73-8; DCPH, 829-84-5; $LiEt_3BH$, 22560-16-3; $LiEt_3BD$, 74540-86-6; $Ph_3C\cdot$, 2216-49-1; Ph_3CBr, 596-43-0; 5-bromo-1-cyclooctene, 4103-12-2; 5-chloro-1-cyclooctene, 1855-55-6; 2-iodo-1-methylcyclopentane, 92285-02-4; 1-heptene, 592-76-7; *cis*-1,2-dimethylcyclopentane, 1192-18-3; *trans*-1,2-dimethylcyclopentane, 822-50-4; 6-deuterio-1-heptene, 80963-54-8; 1-methyl-2-(deuteriomethyl)cyclopentane, 92285-03-5; 2-iodobicyclo[3.3.0]octane, 92285-04-6; cyclooctene, 931-88-4; bicyclo[3.3.0]octane, 694-72-4.

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Preparation and Properties of Quaternary Ammonium and Phosphonium Permanganates

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Received April 6, 1984

General methods for the preparation and purification of quaternary ammonium and phosphonium permanganates have been developed. Solubility studies indicate that these compounds exist in solution as either ion pairs or aggregates with aggregation being promoted by high concentrations, low temperatures, and solvents of low polarity. In general, the greatest solubilities in nonpolar solvents are observed for compounds such as methyltri-*n*-octylammonium permanganate which permit the anions to penetrate the organophilic cations. None of the compounds prepared exhibit high thermal stability; however, both benzyltriethylammonium permanganate and (*p*-fluorobenzyl)tri-*n*-butylammonium permanganate have good shelf lives under cool (room temperature or lower) conditions. The structures of methyltriphenylphosphonium permanganate and *n*-heptyltriphenylphosphonium permanganate have been determined by X-ray diffraction. The former compound is polymorphic with one form orthorhombic, $Pbc2_1$, $Z = 8$, $a = 12.626$ (3) Å, $b = 14.320$ (26) Å, $c = 19.806$ (7) Å, and the other, $P2_1/c$, $Z = 4$, $a = 10.637$ (6) Å, $b = 13.424$ (10) Å, $c = 15.036$ (8) Å, $\beta = 119.44$ (4)°. The latter compound is orthorhombic $P2_12_12_1$, $Z = 4$, $a = 13.122$ (10) Å, $b = 10.801$ (3) Å, $c = 17.154$ (6) Å.

The permanganate anion, when combined with an organophilic cation, becomes a very useful agent for the oxidation of organic compound in nonaqueous solvents.[1] In some procedures the soluble permanganate salts are formed in phase-transfer processes and utilized in situ without isolation.[2–5] In others, the salts are first isolated as semistable solids and then dissolved in the desired solvent.[6–11] *When used under the latter conditions care must be taken to avoid violent thermal decompositions.*[12–14]

The cations most commonly used to solvate permanganate in nonpolar solvents are quaternary ammonium[8,15] or phosphonium[8] ions and polyether complexes (cyclic[16–18] and linear[18,19]). All evidence indicates that these compounds exist as ion pairs when dissolved in organic solvents.[20]

[†] Observed and calculated structure amplitudes are available from this author.

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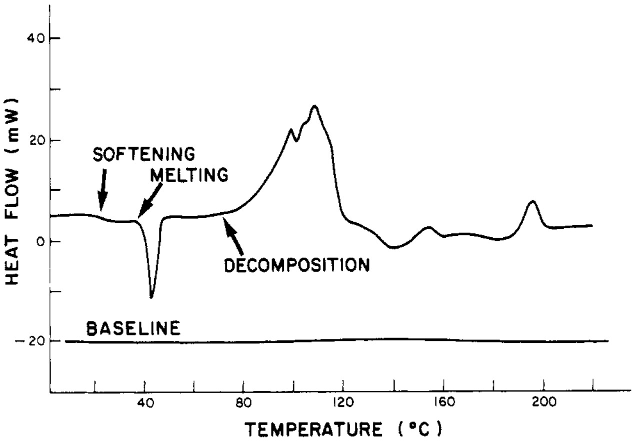

Figure 1. Differential thermal analysis of methyltrioctylammonium permanganate.

As an indication of the growing importance of these reagents in organic syntheses it may be noted that recently reported applications include the oxidation of alkenes,[6,17,18,21-24] alkynes,[26-28] alcohols,[5,30] phenols,[5,31] ethers,[7] sulfides,[32] and amines.[30]

Despite the wide utilization of these compounds no systematic study of their properties has been published. Knowledge of their solubilities, stabilities, and structure is, at present, based primarily on scattered empirical observations. Consequently we have prepared a number of permanganate salts and studied their properties with the expectation that new insights into their fundamental nature will increase their synthetic utility.

Experimental Section

Preparation of Quaternary Ammonium and Phosphonium Permanganates. Two general methods were used for the preparation of these compounds. In one (method A) a quaternary ammonium or phosphonium halide was dissolved in methylene chloride and added to an excess of powdered potassium permanganate. After an exchange of cations had occurred (as indicated by the development of a deep purple color in the solution) the residual solids were removed by filtration and a higher boiling, less polar organic solvent, such as carbon tetrachloride, was added. The solution was then concentrated by drawing over it a stream of dry air. This caused the methylene chloride to evaporate, cooled the solution, reduced its polarity, and initiated crystallization of the permanganate salts.

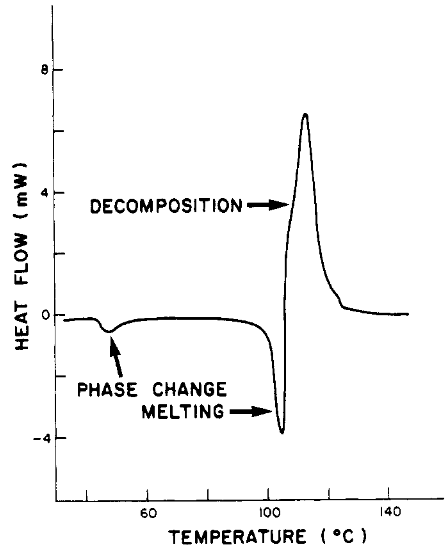

Figure 2. Differential thermal analysis of *n*-hexadecyltrimethylammonium permanganate.

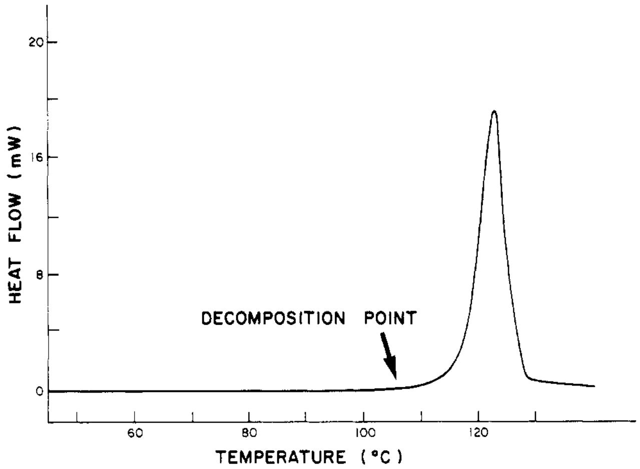

Figure 3. Differential thermal analysis of methyltriphenylphosphonium permanganate.

In the other procedure (method B), concentrated aqueous solutions of the quaternary ammonium halide and potassium permanganate were mixed and the product which precipitated was collected and purified as described above. Some properties of the products are summarized in Table I.

Solubility Measurements. Solubilities were determined by estimating the concentration of saturated solutions spectrophotometrically. Previous work[19] has shown that the extinction coefficient at λ_{max} 526 nm is approximately constant in all solvents. A redetermination with analytically pure[33] tetra-*n*-propylammonium permanganate gave a value for ϵ of 2530 ± 30 L mol^{-1} cm^{-1} and this constant was used throughout.

All solvents (methylene chloride, chloroform, toluene, carbon tetrachloride, and pentane) were first treated overnight with benzyltriethylammonium permanganate and then distilled. For those salts which have high solubilities, a small test tube (3 × 50 mm) was loosely filled with the compound, the appropriate solvent was added, and the resulting concentrated solution thermostated in a water bath at 25 °C. It was then shaken for about one minute, centrifuged, diluted to a concentration that could be measured spectrophotometrically, and filtered through glass wool (to remove any traces of MnO_2) before making absorbance measurements. For those compounds having low solubilities the dilution process was unnecessary.

Differential Thermal Analysis. The decomposition temperatures which are reported in Table I were determined by

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Table I. Properties of Quaternary Ammonium and Phosphonium Permanganates

cation	method	NMR, ppm[a]	dec temp, °C
tetraethylammonium	B (17%)	1.50 (t), 3.65 (q)	113
tetra-*n*-propylammonium	B (97%)	3.40, 2.05, 1.00	104
tetra-*n*-butylammonium	B (89%)	0.35, 0.80, 2.70	98
tetra-*n*-pentylammonium	B (97%)	0.45, 0.90, 2.75	92
tetra-*n*-hexylammonium	A (93%)	0.65, 1.10, 2.95	
tetra-*n*-heptylammonium	A (87%)	0.65, 1.10, 2.90	91
tetra-*n*-octylammonium	A (60%)	0.75, 1.20, 3.05	90
methyltri-*n*-butylammonium	B (88%)	0.05, 0.50, 2.20	107
methyltri-*n*-octylammonium	A (60%)	0.50, 0.95, 2.70	66
n-butyltri-*n*-propylammonium	B (92%)	0.50, 1.20, 2.75	104
benzyltriethylammonium	A (80%)	1.55 (t), 3.40 (q), 4.60, 7.65	114
benzyltri-*n*-butylammonium	B (97%)	0.45, 2.10, 3.80, 6.95	101
n-hexadecyltrimethylammonium	B (78%)	0.90 (t), 1.30, 1.80, 3.40	98[b]
(*p*-nitrobenzyl)tri-*n*-butylammonium	A (90%)	*c*	
(*p*-fluorobenzyl)tri-*n*-butylammonium	A (74%)	0.50, 2.40, 6.60	96
(*p*-fluorobenzyl)triethylammonium	B (68%)	1.45, 3.35, 4.50, 7.50	109
methyltriphenylphosphonium	B (91%)	2.80, 7.80	102
ethyltriphenylphosphonium	B (97%)	1.55, 3.30, 8.00	89
n-propyltriphenylphosphonium	B (98%)	0.85, 1.30, 2.90, 7.55	94
n-butyltriphenylphosphonium	B (98%)	0.85, 1.30, 2.90, 7.55	70
n-pentyltriphenylphosphonium	B (92%)	0.20, 0.85, 2.60, 7.20	68
n-hexyltriphenylphosphonium	B (91%)	−0.10, 0.75, 2.50, 7.10	76
n-heptyltriphenylphosphonium	B (69%)	0.80, 1.25, 1.50, 3.20, 7.75	66
benzyltriphenylphosphonium	B (85%)	2.25, 6.70, 7.20	56
(trichloromethyl)triphenylphosphonium	A (83%)	8.18	86
(2,6-dichlorobenzyl)tris(*p*-chlorophenyl)phosphonium	A (87%)	*c*	64
(*p*-fluorobenzyl)tris(*p*-fluorophenyl)phosphonium	B (86%)	*d*	
(*p*-fluorobenzyl)triphenylphosphonium	B (78%)	*c*	
1,2-ethylenebis(triphenylphosphonium)	B (40%)		
potassium 18-crown-6 complex	A (92%)	3.65	50

[a] Unless otherwise indicated all NMR peaks were broad singlets or multiplets when obtained using a 60-MHz instrument. [b] Melting point 86 °C. [c] Solutions of these compounds were unstable. [d] This product decomposed with a violent explosion.

differential thermal analysis[34] using a duPont 1090 thermal analyzer.[35]

Typical thermograms have been reproduced in Figures 1, 2, and 3. It may be noted that the minimums observed in these curves correspond to melting of the permanganate salts which is an endothermic process. The decomposition, which is an exothermic process, produces a large maximum in the thermograms. The conditions under which these thermograms were obtained are as follows: starting temperature, 25–35 °C; heating rate, 10 °C/min; nitrogen atmosphere; sample size, 3–5 mg; reference, aluminum.

X-ray Crystallography. Methyltriphenylphosphonium permanganate (α form): $C_{19}H_{18}PMnO_4$, $M_r = 377.91$, $Z = 8$, $D_c = 1.420$ g cm^{-3}, μ (Mo Kα) = 8.53 cm^{-1}, $F(000) = 1632$ e. Two forms were found from a crystallographic examination of several crystals. Crystals of the α form predominate in samples crystallized from mixtures of carbon tetrachloride and methylene chloride, rich in the former solvent. The β form predominates in samples crystallized from mixtures rich in methylene chloride. A crystal of the α form with dimensions 0.14 × 0.20 × 0.53 mm was chosen for data collection. Extinction conditions ($0kl$, $k = 2n$; $h0l$, $l = 2n$) and Laue symmetry indicate the space groups *Pbcm* or $Pbc2_1$. Lattice constants ($a = 12.626$ (3) Å, $b = 14.320$ (26) Å, $c = 19.806$ (7) Å) were determined from the positions of 20 strong reflections. The integrated intensities of 3402 independent reflections with $3 \le 2\theta \le 50°$ were measured on a modified Picker diffractometer by using the NRCC diffractometer programs[36] employing line profile analysis. The structure was solved by using the Multan routine in the NRCC crystallographic programs and refined by using XRAY76.[37] Intensities of the three standard reflections showed no systematic trends. Structure amplitudes and normalized structure factors were calculated by standard procedures without absorption corrections. The distribution parameters for the E values correspond very closely to the theoretical values for centrosymmetric space groups. Therefore, structure solution by direct methods was attempted in the space group *Pbcm*, but without success. The Patterson map was examined and it was noted that the Harker peaks corresponding to the mirror plane perpendicular to c were absent. A solution attempted in the noncentrosymmetric space group $Pbc2_1$ was then successful.

The structure was refined by blocked full-matrix least squares with $\sigma(F)^{-2}$ weighting and anisotropic temperature factors. $\sigma(F)$ was based on the counting statistics of the individual reflections with an added contribution derived from the extent by which the scatter in the intensities of the standard reflections exceeded that expected from counting statistics. Refinement for the 1732 independent reflections with $I > 2\sigma(I)$ converged to $R = 0.066$ and $R_w = 0.057$, with a final maximum ratio of shift to error of $^1/_5$. Hydrogen atoms were not included in the structure solutions.

Methyltriphenylphosphonium permanganate (β form): $C_{19}H_{18}PMnO_4$, $M_r = 377.91$, $Z = 4$, $D_c = 1.408$ g cm^{-3}, μ (Mo Kα) = 8.46 cm^{-1}, $F(000) = 816$ e. A crystal of the β form with dimensions 0.10 × 0.22 × 0.45 mm was chosen for data collection. Extinction conditions ($h0l$, $l = 2n$; $0k0$, $k = 2n$) and Laue symmetry indicated the space group $P2_1/c$. Lattice constants ($a = 10.637$ (6) Å, $b = 13.424$ (10) Å, $c = 15.036$ (8) Å, $\beta = 119.44$ (4)°) were determined as for the α form. The integrated intensities of 3312 independent reflections with $3 \le 2\theta \le 50°$ were recorded. Intensities were reduced to structure amplitudes and normalized structure factors as for the α form. The structure was solved by the multisolution direct method and refined as described for the α form. Refinement for 2138 independent reflections with $I > 2\sigma(I)$ converged to $R = 0.080$ and $R_w = 0.090$.

***n*-Heptyltriphenylphosphonium permanganate**: $C_{25}H_{30}PMnO_4$, $M_r = 461.91$, $Z = 4$, $D_c = 1.313$ g cm^{-3}, μ (Mo Kα) = 6.64 cm^{-1}, $F = 1008$ e. A number of crystals were examined; none showed good diffraction characteristics. The best crystal found, with dimensions 0.15 × 0.14 × 0.30 mm, was used for data collection. Extinction conditions ($h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$) and Laue symmetry indicated the space group $P2_12_12_1$.

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Table II. Solubilities of Quaternary Ammonium and Phosphonium Permanganates (*M*)

cation	CH_2Cl_2	$CHCl_3$	$C_6H_5CH_3$	CCl_4	H_2O
tetraethylammonium	0.235	*a*	*b*	*b*	7.30×10^{-2}
tetra-*n*-propylammonium	0.076	*a*	*b*	*b*	3.83×10^{-2}
tetra-*n*-butylammonium	0.417	*a*	3.44×10^{-4}	2.96×10^{-5}	2.10×10^{-3}
tetra-*n*-pentylammonium	0.482	0.221	5.59×10^{-5}	2.42×10^{-5}	9.29×10^{-5}
tetra-*n*-hexylammonium	0.545	0.261	5.81×10^{-5}	3.51×10^{-5}	*b*
tetra-*n*-heptylammonium	0.645	0.339	6.28×10^{-5}	7.48×10^{-5}	*b*
tetra-*n*-octylammonium	0.713	0.604	4.02×10^{-4}	5.93×10^{-4}	*b*
n-hexadecyltrimethylammonium	0.229	0.229	*b*	*b*	1.48×10^{-4}
benzyltriethylammonium	5.76×10^{-2}	4.6×10^{-3}	*b*	*b*	4.97×10^{-3}
(*p*-fluorobenzyl)triethylammonium	1.12	1.47	*b*	*b*	9.35×10^{-3}
n-butyltri-*n*-propylammonium	0.827	0.582	*b*	*b*	4.10×10^{-3}
methyltri-*n*-butylammonium	1.83	1.14	4.23×10^{-4}	5.62×10^{-5}	5.85×10^{-3}
benzyltri-*n*-butylammonium	1.02	1.01	1.05×10^{-4}	*b*	4.98×10^{-4}
(*p*-fluorobenzyl)tri-*n*-butylammonium	0.838	1.12	2.67×10^{-4}	*b*	4.06×10^{-4}
(*p*-nitrobenzyl)tri-*n*-butylammonium	0.551	0.652	8.52×10^{-5}	*b*	1.40×10^{-4}
methyltri-*n*-octylammonium	1.38	1.067	0.798	1.60×10^{-2}	*b*
methyltriphenylphosphonium	1.15	0.941	*b*	*b*	1.17×10^{-3}
ethyltriphenylphosphonium	1.29	1.22	1.58×10^{-5}	*b*	6.27×10^{-4}
n-propyltriphenylphosphonium	0.873	1.03	3.57×10^{-5}	*b*	1.09×10^{-4}
n-butyltriphenylphosphonium	1.16	1.15	3.18×10^{-5}	*b*	3.80×10^{-4}
n-pentyltriphenylphosphonium	1.46	1.56	2.38×10^{-4}	*b*	2.40×10^{-4}
n-hexyltriphenylphosphonium	1.36	1.28	2.02×10^{-4}	*b*	7.63×10^{-4}
n-heptyltriphenylphosphonium	1.36	1.28	2.02×10^{-4}	*b*	7.53×10^{-4}
(trichloromethyl)triphenylphosphonium	0.515	0.424	*b*	*b*	5.84×10^{-4}
benzyltriphenylphosphonium	0.430	9.31×10^{-2}	*b*	*b*	9.37×10^{-5}
(2,6-dichlorobenzyl)tris(*p*-chlorophenyl)phosphonium	0.310	5.70×10^{-2}	*b*	*b*	*b*
18-crown-6	0.813	0.257	1.64×10^{-4}	*b*	3.32×10^{-2}

[a] Unstable solution. [b] Insoluble.

Lattice constants (a = 13.122 (10) Å, b = 10.801 (3) Å, c = 17.154 (6) Å) were determined and integrated intensities of 1831 independent reflections collected as for the methyl compounds. Data collection was terminated when 2θ had reached 46° because the intensities of the three standard reflections had each dropped to roughly $^1/_3$ of their original values. Intensities were reduced to structure amplitudes and normalized structure factors as for the methyl compounds, except that corrections were applied to compensate for the loss of diffracting power. The structure was solved by the multisolution direct method, and refined to $R = 0.10$ and $R_w = 0.126$ using 1530 reflections with $I > 2\sigma(I)$.

Results

Solubilities. The results of the solubility studies have been summarized in Table II. Each determination was done in triplicate with the deviations between individual determinations being 1–3%.

If a permanganate salt is much more soluble in either an organic solvent or the aqueous phase it is difficult to obtain a direct measurement of the distribution coefficient for that particular system. However, this information, which is often of practical importance, may be calculated by use of the reported solubility data. Since the quaternary ammonium permanganates would exist as ion pairs in most organic solvents, but as discrete ions in water,[20] the equilibrium constant controlling the extraction of a salt from water into the organic solvent would be given by eq 1 and 2, which are in turn related to the experimentally determined solubilities by way of eq 3.

$$Q^+{}_{aq} + MnO_4^-{}_{aq} \xrightleftharpoons{K_f} Q^+MnO_4^-{}_{org} \qquad (1)$$

$$K_E = \frac{[Q^+MnO_4^-]_{org}}{[Q^+]_{aq}[MnO_4^-]_{aq}} = \frac{[Q^+MnO_4^-]_{org}}{[MnO_4^-]_{aq}^2} \qquad (2)$$

$$K_E = \frac{\text{solubility of } QMnO_4 \text{ in an organic solvent } (M)}{(\text{solubility of } QMnO_4 \text{ in water})^2\ (M^2)} \qquad (3)$$

However, values of K_E calculated in this way should not be used without reservations for two reasons: (1) Under certain conditions the permanganate salts may exist as aggregates rather than as ion pairs in organic solvents. (2) The properties of an organic solvent may change when it becomes "wet" by being in contact with water. Despite these limitations it was observed that in at least some cases (which were amenable to direct measurement) there is reasonable agreement between the calculated extraction constants and those obtained experimentally. For example, when the extraction constant for benzyltriethylammonium permanganate in methylene chloride–water mixtures was measured experimentally a value of 2010 ± 190 M^{-1} was obtained. This compares very favorably with the calculated value of 2330 ± 120 M^{-1}. On the other hand, the agreement for tetraethylammonium permanganate was not as good. The measured value was 12.6 ± 0.4 as compared to a calculated value of 44 ± 2. However an examination of the NMR spectrum of this compound (as will be discussed later) indicates that it exists partially as an aggregate in methylene chloride. Nevertheless, the two values are of the same order of magnitude and it appears that the data in Table II can be used to obtain a rough estimate of the extraction constants in those cases where they cannot be obtained by direct measurement.

Crystallographic Results. The fractional atomic coordinates, equivalent isotropic temperature factors, and individual anisotropic temperature factors for methyltriphenylphosphonium (α and β forms), and *n*-heptyltriphenylphosphonium permanganates are provided as supplementary material. Detailed information concerning the molecular geometry of each compound is also available as supplementary material. Because of the poor quality of the crystalline material available, it is not unexpected that all three structures are of relatively low accuracy. Nevertheless, the nature of the association between the permanganate ions and the cations is clearly revealed by the packing diagrams (which are also available as supplementary material).

The independent crystallographic units for each compound are shown in Figures 4, 5, and 6.

The α form of the methyl compound contains two formula units within the asymmetric unit of the structure.

Table III. Averages of Similar Bond Lengths in the α and β Form of Methyltriphenylphosphonium and n-Heptyltriphenylphosphonium Permanganate (Å)

	α form molecule 1, av esd,[a] sd[b]	α form molecule 2, av esd,[a] sd[b]	β form, av esd,[a] sd[b]	n-heptyl av esd,[a] sd[b]
C–C(phenyl)	1.40, 0.03, 0.06	1.40, 0.03, 0.07	1.40, 0.02, 0.05	1.40, 0.02, 0.06
C–C(alkyl)				1.50, 0.04, 0.11
P–C(phenyl)	1.77, 0.02, 0.06	1.81, 0.02, 0.04	1.79, 0.01, 0.02	1.82, 0.02, 0.03
Mn–O	1.50, 0.02, 0.04	1.49, 0.02, 0.04	1.54, 0.01, 0.04	1.47, 0.02, 0.09

[a] The estimated standard deviation (esd) of the average is calculated as the average of individual estimated standard deviations of the quantities which are averaged. [b] The standard deviation (sd) of the quantity $\langle b \rangle$, averaged over the n quantities b_i, is calculated as $(\sum (b_i - \langle b \rangle)^2/(n - 1))^{1/2}$.

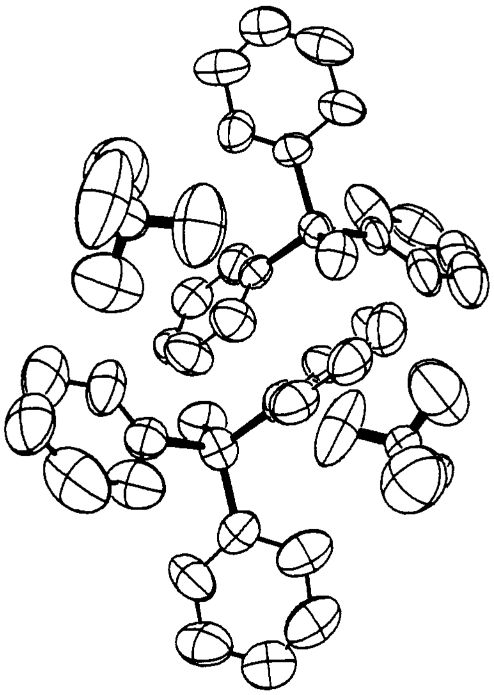

Figure 4. Independent crystallographic unit of methyltriphenylphosphonium permanganate (α form).

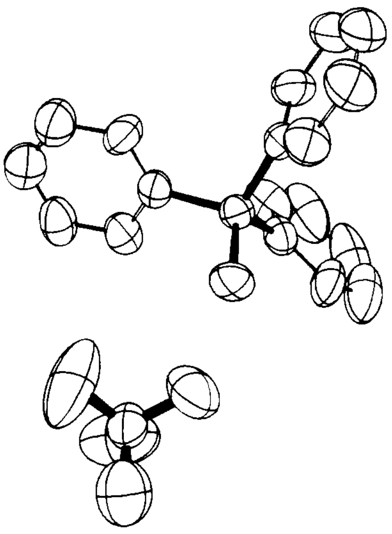

Figure 5. Independent crystallographic unit of methyltriphenylphosphonium permanganate (β form).

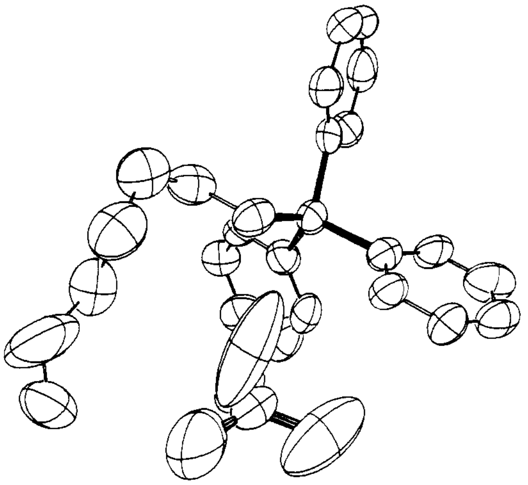

Figure 6. Independent crystallographic unit of n-heptyltriphenylphosphonium permanganate.

This structural unit contains four molecules and appears centrosymmetric to visual inspection, with a local center of symmetry at $x = 0.25$, $y = 0.38$, $z = 0.42$. Upon more careful analysis it becomes evident that the integrity of this center declines with increasing distance from the center of the four-molecule unit and the four-molecule units do not themselves pack to form a centrosymmetric structure.

Table III lists average values for similar bond lengths for the two molecules of the asymmetric unit in the methyl (α and β forms) and the n-heptyl compounds together with estimates of their standard deviations (as determined from $(\sum (b_i - \langle b \rangle)^2/(n - 1))^{1/2}$ where b_i is an individual bond length and $\langle b \rangle$ is an average over n bond lengths of similar type). The table also shows the average of the calculated values of the standard deviations based on the estimated standard deviations of the atomic coordinates obtained from least-squares calculations. The ratio of the former to the latter ranges from 2.2 to 3.0 and averages 2.7. The fact that the standard deviations are estimated to be too small is probably based in part on real differences in the lengths of similar bonds but must also represent systematic error arising from absorption or crystal degradation and other phenomena affecting the collection of data. Nevertheless, the average bond lengths are reasonable.

The anisotropic temperature factors of the oxygen atoms are large, suggesting that the permanganate ions are undergoing substantial librational motion. Because of this motion the average Mn–O bond lengths are shorter than previously reported values (1.63 A) for the potassium and cesium salts.[38] Approximate thermal corrections to the Mn–O bond lengths according to the method of Schomaker and Trueblood[39] average to 0.13 A, thus making the corrected values only slightly less than those reported previously.[38]

Discussion

CAUTION! Whenever quaternary ammonium or phosphonium permanganates are handled, certain precautions are in order. These solids should never be al-

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Table IV. Conformational Parameters for the Cation in the α and β Form of Methyltriphenylphosphonium and *n*-Heptyltriphenylphosphonium Permanganate (deg)[a]

	1	2	3
α form (1)	−16	−31	−66
α form (2)	2	13	70
β form	6	26	77
n-heptyl	11	29	71

[a] These values define the angle at which the plane of each phenyl ring intersects the plane defined by the P–C(alkyl) and P–C-(phenyl) bonds.

Table V. The Four Shortest [P•••O] Contact Distances in Methyltriphenylphosphonium and *n*-Heptyltriphenylphosphonium Permanganate (Å)[a]

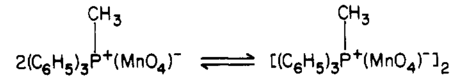
	1	2	3	4
α form (1)	4.28 (2)	4.46 (2)	4.57 (2)	4.74 (3)
α form (2)	3.94 (2)	4.41 (2)	4.62 (2)	4.73 (2)
β form	3.94 (1)	4.00 (1)	4.02 (1)	4.88 (1)
n-heptyl	4.31 (2)	4.81 (1)	5.37 (3)	5.57 (3)

[a] esd in parentheses.

lowed to stand in a warm place and care must be exercised when they are being transfered from one vessel to another.

The observed propeller-like geometry of the alkyltriphenylphosphonium cations is not unusual.[40-45] In each of the four examples one phenyl ring is approximately parallel to the P–C (alkyl) bond, another is inclined by 13°–31° and the third is rotated 66°–77° from the reference plane (Table IV). The packing diagrams show that the cations are surrounded by four anions, each associated with (but not centered on) a face of the tetrahedron produced by the quaternary phosphorus atoms. The [P···O] distances for each structure, which have been summarized in Table V, show that one of the permanganate ions is distinctly closer than the other three to the phosphorus atom of the *n*-heptyltriphenylphosphonium cation. This is the permanganate ion which is "nestled" under the *n*-heptyl chain as shown in Figure 6. Such penetration effects, which have long been suspected to be of importance to compounds of this type,[46,47] may be responsible for some of the solubility differences seen in Tables II and III. For example, *n*-heptyltriphenylphosphonium permanganate is more soluble in nonpolar solvents than is methyltriphenylphosphonium permanganate, while the converse is true for the very polar solvent, water. Similar (but more exaggerated) effects are observed when one compares the solubility of ammonium salts such as methyltri-*n*-butylammonium permanganate and methyltri-*n*-octylammonium permanganate with the corresponding symmetrical tetraalkyl cations. Observed changes in reaction rates when these permanganate salts are used as oxidants are also believed to be associated with the ability of the anion to penetrate the hydrocarbon shell surrounding the positive center of the cation.[47]

Assuming that the interionic distances obtained from the crystallographic studies would also approximately pertain to methyltriphenylphosphonium permanganate in solution, it would (according to the theory advanced by Brandstrom[20]) exist as an ion pair or an aggregation of ion pairs[48-51] in organic solvents of low polarity. The degree of aggregation, which would be expected to be directly proportional to the concentration of the salt and inversely proportional to the polarity of the solvent,[51-55] may be responsible for the formation of the two crystal modifications of methyltriphenylphosphonium permanganate. As described above, crystals of the α form were obtained from a dichloromethane–carbon tetrachloride mixture rich in carbon tetrachloride, while the β form was obtained from a mixture rich in dichloromethane. It is possible that methyltriphenylphosphonium permanganate exists in these solvents as a mixture of ion pairs and ion quadrupoles in equilibrium as depicted in eq 4.



$$2(C_6H_5)_3\overset{CH_3}{P^+}(MnO_4)^- \rightleftharpoons [(C_6H_5)_3\overset{CH_3}{P^+}(MnO_4)^-]_2 \qquad (4)$$

When the solution is rich in the nonpolar solvent, carbon tetrachloride, the quadrupole species may dominate and the α form, which contains two methyltriphenylphosphonium permanganate ion pairs in an asymmetric unit, would crystallize from the solution. On the other hand, when the solvent mixture is rich in dichloromethane, the single ion pair would be the dominant species and the β form, which contains only one ion pair in an asymmetric unit, could crystallize out. Both (*p*-fluorobenzyl)tributylammonium and tetrabutylammonium permanganate also exhibited two different crystal modifications. However, the relative instability of these compounds at room temperature prevented us from attempting a crystallographic study of their structures.

An examination of the ^1H NMR spectra of the quaternary ammonium and phosphonium permanganates has provided evidence that both concentration and solvent polarity are of possible importance with respect to the formation of aggregates. For example, the spectrum of tetraethylammonium permanganate is well resolved in D_2O, less well resolved in acetone-d_6 (a polar organic solvent), and unresolved in CD_2Cl_2 (a much less polar organic solvent). Thus it appears to exist as discrete ions in D_2O, as solvent-separated ion pairs in acetone-d_6 and as intimate ion pairs or aggregates in CD_2Cl_2. The broadening observed in the least polar solvent would result if the rate of formation and dissociation of the aggregates was similar to the NMR time scale.[56,57]

The effect of concentration and temperature on the formation of aggregates was also illustrated by a study of ^1H NMR spectra of methyltriphenylphosphonium permanganate under various conditions. In the polar solvent, acetone-d_6, the methyl protons appeared as a doublet at 2.55, $J(^{31}P\text{–}CH) = 13.2$ Hz.[58] However, in CD_2Cl_2 the

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doublet collapsed into a broad singlet indicating the formation of aggregates.

When the spectrum of a very dilute solution of methyltriphenylphosphonium permanganate in CD_2Cl_2 was obtained at 40 °C the methyl doublet was again apparent, indicating that at lower concentrations this compound also exists as discrete ions or as solvent-separated ion pairs even in nonpolar solvents. However, when the temperature was decreased the doublet was transformed into a very broad singlet showing that a decrease in temperature can also promote formation of aggregates in nonpolar solvents.

One additional aspect of the spectral properties of the compounds reported in Table I merits further comment. It may be noted that the chemical shifts for the alkyl hydrogen atoms are often unusually small. This must be caused by the presence of the permanganate ions because similar effects have not been observed to occur with other anions. Although the exact reason for these upfield shifts has not been identified, it is of interest to note that they are greatest for those ion pairs where other evidence indicates that penetration is important. For example, methyltri-*n*-butylammonium permanganate exhibits both the lowest chemical shifts and the highest solubility of the permanganates studied. Both of these effects are consistent with the formation of tight ion pairs if it is realized that the presence of a permanganate ion near a hydrogen atom can influence its electron density either by a direct field effect or by diamagnetic anisotropic effects.

When attention is focused on the solubilities of these compounds at least two important factors much be given consideration: (i) the lattice energy of the solid, and (ii) the solvation energy of the solute. An increase in the size of the quaternary ammonium or phosphonium cations may be expected to decrease the lattice energy of the solid (by increasing the distance between unlike charges[59]) and to increase the solvation energy in nonpolar solvents (by immersion of the charge in a larger volume of nonpolar ligands). An examination of the solubility data summarized in Table II indicates that this principle is of major importance in determining the solubility of permanganate salts in organic solvents. However, a close inspection of the results reveals several other subtle effects associated with the structures of the cations and the nature of the solvents. For example, the obviously higher solubilities in methylene chloride and chloroform as compared to carbon tetrachloride and toluene are likely due to the greater polarity of the former.[60] The effect, while somewhat muted for those ion pairs where penetration is an important phenomenon, is most apparent for the smaller, least organophilic cations. The slightly higher solubilities in methylene chloride as compared to chloroform are also likely due to the greater polarity of the former solvent.[60] However, the ability of chloroform to hydrogen bond to fluorine and oxygen compounds[60] sometimes causes the solubilities to be enhanced in that solvent.[61] For example, (*p*-fluorobenzyl)triethylammonium, (*p*-fluorobenzyl)tributylammonium, and (*p*-nitrobenzyl)tributylammonium permanganates are actually more soluble in chloroform than in methylene chloride.

Extraction constants, calculated from the data of Table II, are an empirical guide to the selection of an appropriate agent for phase-transfer assisted oxidations.[1-5] Unfortunately, because of the aforementioned multitude of factors that can influence the magnitude of these constants they are not readily amenable to any comprehensive mathematical analysis. However, as the data in Table VI indicates, a limited number of these extraction constants can be described by eq 5, where *a*, *b*, and *c* are constants, *n* is the total number of aliphatic carbon atoms in the cation, and *m* is the total number of aromatic carbon atoms.

$$\log K_E = an + bm + c \qquad (5)$$

Application of this equation, which is similar to one previously used to correlate distribution coefficients,[2,62] gives similar values for *a* and *b* (0.49 and 0.41, respectively) thus suggesting that aliphatic and aromatic carbon atoms contribute in roughly equal proportions to the solubility properties of these compounds.

Table VI. Experimental and Calculated Values of log K_E for Some Quaternary Ammonium Permanganates[a]

cation	aliphatic C	aromatic C	expt	from eq 5
tetraethylammonium	8	0	1.64	1.58
benzyltriethylammonium	7	6	3.37	3.55
tetra-*n*-propylammonium	12	0	3.71	3.54
tetra-*n*-butylammonium	16	0	4.97	5.50
benzyltri-*n*-butylammonium	13	6	6.61	6.49
tetra-*n*-pentylammonium	20	0	7.71	7.46

[a] Extraction constants are defined by eq 3 (Table II) for the solvents methylene chloride and water.

The thermal stability of quaternary ammonium and phosphonium permanganates is also a matter of concern. Although we have never experienced any serious difficulties in handling or storing these compounds, other workers have reported that under certain conditions decompositions with explosive forces may occur.[12-14] Consequently the question of stability is of importance to the safe use of these compounds in chemical reactions and it is the factor which will ultimately determine the viability of quaternary ammonium and phosphonium permanganates as commercial products.

When heated in a melting point tube, decomposition occurs at a specific temperature for each compound. The decomposition is accompanied by a puff of smoke and a small flame which flares from the open end of the tube. In an attempt to find safe ways of storing these compounds we also studied the effects of heating them in a nitrogen atmosphere and under vacuum. Unfortunately, in both instances the decomposition process remained visually unaltered. Consequently, it appears that the oxygen which is consumed in the fire must come from permanganate itself. This is consistent with the results that have been reported from studies on the decomposition of inorganic permanganates. In each case oxygen was one of the products.[63]

Some indication of a possible mechanism for these decompositions may be gleaned from a comparison with the results obtained when quaternary ammonium and phosphonium salts of other oxidizing anions, such as perchlorate, pirate, and nitrate, were decomposed under controlled conditions.[64] The decompositions have been explained in terms of the dissociation of these salts prior to their decomposition;[65] i.e., perchloric acid was detected

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during the decomposition of quaternary ammonium perchlorates. This suggests that decomposition may be initiated by transfer of a proton from the cation to the anion. If a similar mechanism were to pertain for the permanganates, the observed ignitions would be in agreement with the violent oxidative nature of permanganic acid. It has been observed that HMnO$_4$ reacts explosively when brought into contact with any type of organic material.[66]

One of the objectives of this work was to prepare an inexpensive quaternary ammonium or phosphonium permanganate that had good solubility properties and was at the same time stable enough to be safely handled. Our studies have led us to the conclusion that, by use of the procedures described herein, several such compounds can be easily prepared. When using any of these compounds, however, precautions are in order. The solids should be held in cold storage at all times and care should be exercised whenever they are being handled.

For long term shelf stability, benzyltriethylammonium permanganate seems to be the best choice despite the fact that it has been reported to be an explosive compound.[13,14] We have stored this compound in our laboratory in solid form for over two years without any problems. Methyltriphenylphosphonium permanganate may be considered as a second choice, but it is expensive to prepare when compared with the benzyltriethylammonium salts. In the interest of maximum laboratory safety it is recommended that no attempt be made to store large amounts of these potentially explosive compounds.[12–14]

For very slow reactions, which take several days to complete, (*p*-fluorobenzyl)tributylammonium permanganate may be suggested because it has very good stability in solution. However, the corresponding quaternary ammonium halide is not available commercially thus making its preparation more time consuming and expensive.

In dichloromethane, which appears to be the best solvent for these compounds,[5] the solubility of benzyltriethylammonium permanganate seems to be sufficient. However, in highly nonpolar solvents (such as carbon tetrachloride) methyltri-*n*-octylammonium permanganate should be used because of its greater solubility. When all of the various factors such as solubility, stability, cost, and reactivity are taken into consideration, the use of benzyltriethylammonium permanganate in methylene chloride would be recommended for most preparative purposes.

Acknowledgment. The authors gratefully acknowledge financial assistance from the Natural Science and Engineering Research Council of Canada, Imperial Oil Limited, and the Carus Chemical Company.

Registry No. QMnO$_4$ (Q = tetraethylammonium), 76710-78-6; QMnO$_4$ (Q = tetra-*n*-propylammonium), 35638-40-5; QMnO$_4$ (Q = tetra-*n*-butylammonium), 35638-41-6; QMnO$_4$ (Q = tetra-*n*-pentylammonium), 35638-41-6; QMnO$_4$ (Q = tetra-*n*-hexylammonium), 35638-43-8; QMnO$_4$ (Q = tetra-*n*-heptylammonium), 34293-34-0; QMnO$_4$ (Q = tetra-*n*-octylammonium), 82444-41-5; QMnO$_4$ (Q = methyltri-*n*-butylammonium), 82444-42-6; QMnO$_4$ (Q = methyltri-*n*-octylammonium), 82444-43-7; QMnO$_4$ (Q = *n*-butyltri-*n*-propylammonium), 92282-95-6; QMnO$_4$ (Q = benzyltriethylammonium), 68844-25-7; QMnO$_4$ (Q = benzyltri-*n*-butylammonium), 60754-79-2; QMnO$_4$ (Q = *n*-hexadecyltrimethylammonium), 73257-07-5; QMnO$_4$ (Q = (*p*-nitrobenzyl)-tri-*n*-butylammonium), 92282-96-7; QMnO$_4$ (Q = (*p*-fluorobenzyl)tri-*n*-butylammonium), 92282-97-8; QMnO$_4$ (Q = (*p*-fluorobenzyl)triethylammonium), 92282-98-9; QMnO$_4$ (Q = methyltriphenylphosphonium), 73335-41-8; QMnO$_4$ (Q = ethyltriphenylphosphonium), 92282-99-0; QMnO$_4$ (Q = *n*-propyltriphenylphosphonium), 92283-00-6; QMnO$_4$ (Q = *n*-butyltriphenylphosphonium), 92283-01-7; QMnO$_4$ (Q = *n*-pentyltriphenylphosphonium), 92283-02-8; QMnO$_4$ (Q = *n*-hexyltriphenylphosphonium), 92283-03-9; QMnO$_4$ (Q = *n*-heptyltriphenylphosphonium), 92283-04-0; QMnO$_4$ (Q = benzyltriphenylphosphonium), 92283-05-1; QMnO$_4$ (Q = (trichloromethyl)triphenylphosphonium), 92283-06-2; QMnO$_4$ (Q = (2,6-dichlorobenzyl)tris(*p*-chlorophenyl)phosphonium), 92283-07-3; QMnO$_4$ (Q = (*p*-fluorobenzyl)tris(*p*-fluorophenyl)phosphonium, 92283-08-4; QMnO$_4$ (Q = (*p*-fluorobenzyl)triphenylphosphonium, 92283-09-5; Q(MnO$_4$)$_2$ (Q = 1,2-ethylenebis(triphenylphosphonium), 76710-76-4; QMnO$_4$ (Q = potassium 18-crown-6 complex), 74218-78-3; KMnO$_4$, 7722-64-7.

Supplementary Material Available: Packing diagrams and tables containing infrared data, final least-squares, positional and thermal parameters, details of the molecular geometry, and the equation of least-squares planes for α and β forms of methyltriphenylphosphonium and *n*-heptyltriphenylphosphonium permanganates (25 pages). Ordering information is given in any current masthead page.

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Absolute Configuration of Multifidene as Deduced by Total Synthesis of the Unnatural Levorotatory Enantiomer

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Received April 30, 1984

The powerful sperm attractant of the brown alga *Cutleria multifida*, (+)-multifidene (**1**), is shown to possess the 3*S*,4*S* configuration. The protocol, which parallels our earlier synthesis of the racemic polyolefinic hydrocarbon, begins with (−)-*cis*-(5-vinyl-2-cyclopentenyl)acetic acid (**2**) of known absolute configuration. Thus, the stereogenic nature of (+)-**1** is identical with that of the naturally occurring prostaglandins.

Sexual reproduction by the brown alga *Cutleria multifida* is recognized to originate by release of a pheromone bouquet by mature female gynogametes.[1] The active component of this luring substance has been identified as

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