

SOME COMMENTS ON THE THERMAL STABILITY OF SUBSTITUTED AMMONIUM, PHOSPHONIUM,
AND ARSONIUM PERMANGANATES AND THEIR USE IN ALKANE OXIDATION

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SUMMARY Tetraethyl- and tetrabutylammonium permanganate are less prone to explosive decomposition when heated than are benzyl(triethyl)ammonium and methyl-(triphenyl)phosphonium permanganate and are about equally effective as oxidants for the conversion of alkanes into alcohol and ketones.

Following the recent report by Schmidt and Schäfer¹ that benzyl(triethyl)ammonium permanganate (1) is an efficient oxidant for the conversion of alkanes and arylalkanes into alcohols and ketones under mild conditions in non-aqueous media, we attempted to use the reagent as a means of regioselective hydroxylation of the diamondoid hydrocarbons diamantane and triamantane. The salt was prepared as described by Schmidt and Schäfer, but was found to undergo violent decomposition when dried at 80-90°C. Subsequently, Schmidt and Schäfer,² and independently Jäger, Lütolf, and Meyer,³ described more recent experiences with benzyl-(triethyl)ammonium permanganate and drew attention to the hazards associated with working with the crystalline material. Our own experiences working with quite small quantities confirm that the substance is very unstable and should be handled with care.

The considerable synthetic potential of this type of reagent for controlled oxidation of alkanes under mild conditions led us to search for suitable, safer alternatives. Accordingly, several new permanganate salts (Table 1) were prepared, using the reaction of aqueous potassium permanganate with the

appropriate ammonium, phosphonium, or arsonium bromide, and dried carefully at or near room temperature. Stability tests in which small samples of each salt

Table 1 Some Ammonium, Phosphonium, and Arsonium Permanganates

$\text{PhCH}_2(\text{CH}_3\text{CH}_2)_3\text{NMnO}_4$ (1)	$\text{Ph}_4\text{AsMnO}_4$ (6)
$\text{PhCH}_2(\text{CH}_3)_3\text{NMnO}_4$ (2)	$(\text{CH}_3\text{CH}_2)_4\text{NMnO}_4$ (7)
$\text{Ph}_3\text{PCH}_3\text{MnO}_4$ (3)	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{NMnO}_4$ (8)
$\text{Ph}_3\text{PCH}_2\text{CH}_2\text{PPh}_3\text{MnO}_4$ (4)	$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{MnO}_4$ (9)
$\text{CH}_3(\text{CH}_2)_{15}\text{NC}_5\text{H}_5\text{MnO}_4$ (5)	

in a capillary tube were heated at 2°C per minute revealed that compounds (1)-(5) all decomposed with explosive violence when the temperature reached 80-90°C; the arsonium salt (6) also decomposed explosively, but not until the temperature reached 120-130°C. Compounds (7)-(9), on the other hand, showed no explosive tendency, but they did decompose passively between 80 and 100°C. This contrasting behaviour may be associated with the fact that compounds (1)-(6) all contain unsaturation in the cation whereas compounds (7)-(9) do not. However, the explosion hazard with the former can be diminished very substantially by adsorbing them on alumina. Thus, addition of chromatography grade alumina (4g) to a stirred dichloromethane solution (100 ml) of benzyl(triethyl)ammonium permanganate (1g) followed by evaporation of the solvent gave a dispersed form of the oxidant which did not explode when heated, though it did undergo slow decomposition.

Oxidation studies, performed in glacial acetic acid for 8-10 hours at 35-40°C using a 1.0:1.1 molar ratio of substrate to oxidant, revealed that over a range of alkane structures (Tables 2-4) tetraalkylammonium permanganates are generally about as efficient as oxidants as their arylammonium, arylphosphonium, or arylarsonium counterparts. trans-Decalin was used to probe differences between representative members of the saturated and unsaturated series. The results in Table 2 indicate that the tetrabutylammonium salt (8) is in fact a more efficient oxidant than benzyl(triethyl)ammonium permanganate (1) and is comparable to methyl(triphenyl)phosphonium permanganate (3) in its ability to selectively oxidise trans-decalin to trans-9-decalol. Within the saturated series (Table 3) tetrabutylammonium permanganate is generally more effective than the tetraethyl- salt as an oxidant towards cis-decalin, methylcyclohexane, cumene, and tetralin. All nine permanganates are effective agents for bridge-head hydroxylation of diamantane (10) and triamantane (13) (Table 4), though here the saturated members are slightly less efficient than their more

Table 2 Oxidation of Trans-Decalin with Permanganates (1),(3),(7) and (8)⁴

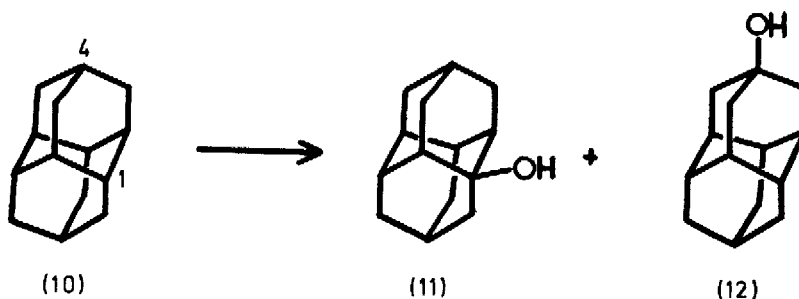
<u>Oxidant</u>	<u>trans-9-Decalol (%)</u>	<u>trans-1-Decalone (%)</u>	<u>trans-2-Decalone (%)</u>
1	30 (11) ^a	28 (13) ^a	13 (3) ^a
3	70	15	3
7	24	11	4
8	65	15	3

a. percentages in brackets are those reported in reference 1.

Table 3 Oxidation of Alkanes with Permanganates (7) and (8)⁴

<u>Alkane</u>	<u>Oxidant</u>	<u>Products (%)</u>
<u>cis-Decalin</u>	7	<u>cis-9-Decalol</u> (20)
<u>cis-Decalin</u>	8	<u>cis-9-Decalol</u> (14) + Unidentified (3)
Methylcyclohexane	7	<5% Oxidation
Methylcyclohexane	8	1-Methylcyclohexanol (20) + 2-Methylcyclohexanone (3)
Cumene	7	2-Phenyl-2-propanol (5) + Acetophenone (5)
Cumene	8	2-Phenyl-2-propanol (20) + Acetophenone (5)
Tetralin	7	<5% Oxidation
Tetralin	8	1-Tetralone (28)

hazardous counterparts. However, benzyl(triethyl)ammonium permanganate dispersed on alumina is about as effective as the unsupported salt for hydroxylation of the 1-position of diamantane and the 3 and/or 4 position of triamantane.⁵ Very similar preferences have been observed in the hydroxylation of these systems using lead tetrabenzoate⁶ and para-nitroperbenzoic acid.⁷



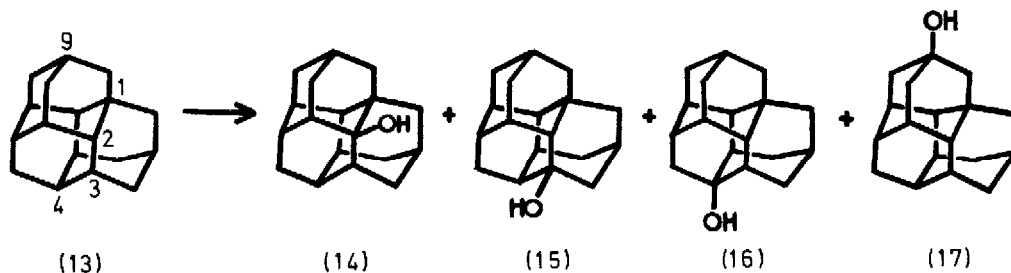


Table 4 Products of Oxidation of Diamantane (10) and Triamantane (13)⁴

<u>Oxidant</u>	<u>From Diamantane (%)</u>		<u>From Triamantane (%)</u>		
	(11)	(12)	(14)	(15)/(16)	(17)
1	38	7	14	36	10
1 on alumina	46	8	13	38	9
2	54	5	10	31	9
3	47	9	10	21	9
4	28	6	9	28	9
5	32	11	12	20	6
6	31	7	15	39	11
7	15	5	7	18	5
8	26	8	4	12	4
9	31	13	12	20	6

References and Footnotes

1. H.J. Schmidt and H.J. Schäfer, Angew.Chem.Int.Ed.Engl., 1979, **18**, 68.
2. H.J. Schmidt and H.J. Schäfer, Angew.Chem.Intd.Ed.Engl., 1979, **18**, 787.
3. H. Jäger, J. Lütolf, and M.W. Meyer, Angew.Chem.Int.Ed.Engl., 1979, **18**, 786.
4. Product distributions were measured chromatographically.
5. The 3 and 4 isomers of triamantanol are only partially resolved under the chromatographic conditions used.
6. F. Hollowood, A. Karim, M.A. McKervey, P. McSweeney, and H. Duddeck. J.C.S.Chem.Comm., 1978, 306.
7. M.A. McKervey and P. McSweeney, unpublished observations.

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