

A Comparative Study of the Oxidation of Oct-1-ene by Mercury(II), Thallium(III), and Lead(IV) Acetates in Methanol

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A comparative study has been made of the oxidation by mercury(II), thallium(III), and lead(IV) acetates of a mono-substituted aliphatic olefin (oct-1-ene) in methanol. Reaction proceeds in two stages. In the first step, electrophilic addition occurs to give an organometallic adduct in which a methoxy-group is incorporated at C-2. There is no evidence for concerted addition of the two substituents. The adduct from mercury(II) is essentially stable under the reaction conditions but those from thallium(III) and lead(IV) decompose in three competing ways: (i) an acetate group is transferred from the metal atom to C-1 in an S_N1 process; (ii) a carbonium ion is generated on heterolysis of the carbon-metal bond and this undergoes competitive hydride shift and nucleophilic attack; (iii) anchimeric assistance to heterolysis is provided by the neighbouring methoxy-substituent which preferentially migrates to C-1 on collapse of the resultant ion-pair. The relative importance of these three processes is governed by the leaving-group capacity of the metal substituent and by the nature of the ligands on the metal.

It has frequently been noted that the acetates of lead(IV), thallium(III), and mercury(II) show some resemblance to each other in their reaction with olefins.¹⁻⁸ This similarity has been adduced from a comparison of the results obtained by different workers, the conditions employed varying widely. All three instances in which a direct comparison has been made under relatively

¹ (a) R. Criegee, in 'Oxidation in Organic Chemistry. Part A,' ed. K. B. Wiberg, Academic Press, New York, 1965, p. 277; (b) R. M. Moriarty, in 'Selective Organic Transformations,' ed. B. S. Thyagarajan, Wiley, New York, 1972, p. 183.

² R. J. Ouellette, in 'Oxidation in Organic Chemistry, Part B,' ed. W. S. Trahanovsky, Academic Press, New York, 1973, p. 135.

³ H.-J. Kabbe, *Annalen*, 1962, **656**, 204.

constant conditions^{3,4} have been concerned with the behaviour of cyclic olefins. Two of these employed conditions which, in the light of our present understanding of these oxidations, may well have been too drastic⁴ (for instance, at the high temperatures employed, decomposition of organometallic adducts can occur, and

⁴ C. B. Anderson and S. Winstein, *J. Org. Chem.*, 1963, **28**, 605; J. B. Lee and M. J. Price, *Tetrahedron*, 1964, **20**, 1017.

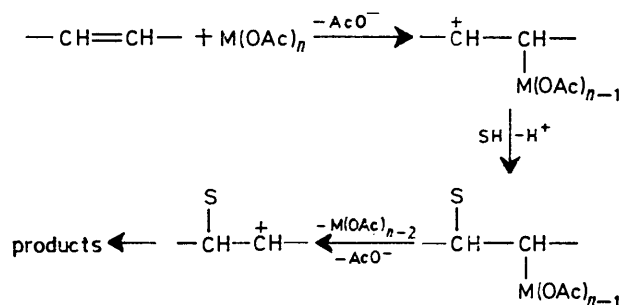
⁵ K. C. Pande and S. Winstein, *Tetrahedron Letters*, 1964, 3393.

⁶ W. Kitching, *Organometallic Chem. Rev.*, 1968, **3**, 61.

⁷ A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1973, **95**, 3635.

⁸ A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1973, 2763.

some of the products obtained would be expected to react further). However, valuable conclusions can be drawn from the classic study by Kabbe.³ His results support the view, originally propounded by Criegee,⁹ that electrophilic addition of the metal acetate to the olefin first occurs. In the case of lead(IV) the resultant adduct rapidly decomposes; the thallium(III) adduct, though very labile, can, under favourable circumstances, be isolated; and the mercury(II) adducts are quite stable. This general scheme is outlined in Scheme 1 where SH is a nucleophilic solvent. The finer details of the scheme have, however, never been elucidated.



SCHEME 1 M = Hg, Tl, or Pb; $n = 2-4$

As part of a comparative study of these three oxidants we have investigated their reactions with simple acyclic olefins in an attempt to optimise conditions for the formation of particular products. Here we report the results of oxidation of oct-1-ene in methanol. The choice of solvent was based on two considerations. First, a study of lead(IV) reactions in less polar solvents such as acetic acid or benzene is complicated by the fact that this oxidant can react with olefins by radical as well as ionic routes and the same products can be obtained from the two reactions.¹⁰⁻¹² A highly polar solvent should favour ionic reactions, so that radical pathways might become of negligible importance. Secondly, we particularly wanted to encourage carbonium-ion rearrangements since this would provide an extra parameter for elucidating the mode of decomposition of the organometallic adduct. A more polar solvent should favour unimolecular reactions leading to carbonium ions and so, probably, increase the extent of migration. Such a process would also be aided by the presence on C-2 of a methoxy-substituent in place of the acetoxy one obtained if acetic acid is employed as solvent since the former can more effectively stabilise the rearranged carbonium ion.

RESULTS AND DISCUSSION

Oct-1-ene in dry methanol was added to a solution of the metal acetate in the same solvent at 60° and the mixture kept at that temperature until no oxidant remained. The lead(IV) and thallium(III) oxidations

⁹ R. Criegee, P. Dimroth, K. Noll, R. Simon, and C. Weis, *Chem. Ber.*, 1957, **90**, 1070.

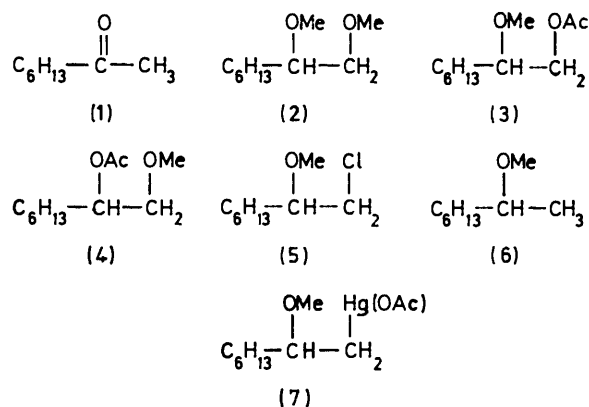
¹⁰ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1967, 771.

¹¹ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1968, 994.

were worked up in the usual way^{10,11,13} before analysis by g.l.c. mass-spectrometry. The mercury(II) reaction, however, was expected to result in an organomercurial adduct which would not be amenable to g.l.c. The crude reaction product was accordingly reduced with sodium borohydride before analysis.

With the first two oxidants five products were obtained, three of which, (1), (2), and (4), were identified by comparison with authentic samples. The structures of the other two, (3) and (5), were assigned on the basis of their mass spectra. Compound (3) has a negligible molecular ion, the first significant fragment occurring at m/e 142 ($M - \text{AcOH}$). The principal structure-determining fragments arise by the typical ether cleavage adjacent to the methoxy-substituent, m/e 129 from loss of AcOCH_2^+ and 117 from loss of $\text{C}_6\text{H}_{13}^+$. The further fragmentation of these two ions accounts for the other major peaks in the spectrum and confirms the presence of a methoxy-group in each. Compound (5) shows no molecular ion but α -cleavage leads to m/e 129 ($M - \text{ClCH}_2$) and 93/95 ($M - \text{C}_6\text{H}_{13}$). The mercury(II) oxidations gave only the single product (6) expected of reduction of the adduct (7).

The results are summarised in Table 1. The chloro-methoxy-adduct (5) is almost certainly formed by electrophilic chlorination of the olefin, the chlorine originating from oxidation of chloride ion impurity by the metal oxidant. Such behaviour has been observed before^{13,14} and is not discussed further.



The first feature of note is the order of reactivity. The rate of consumption of the oxidants would be expected^{2,7} to be $\text{Hg(OAc)}_2 > \text{Tl(OAc)}_3 > \text{Pb(OAc)}_4$ yet we are observing an order in which lead(IV) is intermediate between mercury(II) and thallium(III). We considered two possible explanations of this anomaly. First, the reactions are two-step processes [reaction (1)]. The time noted in Table 1 for oxidation by mercury(II) acetate is dependent solely on k_1 . Formation of the adduct is irreversible under our conditions since, starting from pure (7) in a check experiment, no oct-1-ene or

¹² A. A. Mahmood, D.Phil. Thesis, University of York, 1970.

¹³ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1970, 421.

¹⁴ A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1973, 35.

mercury(II) acetate could be detected. k_2 is also negligible: after 14 days at the reflux temperature only a 2% yield of decomposition product [solely (3)] was obtained. Reaction time for the other two oxidants is, however, a composite figure for the two stages. Intermediate adducts of lead(IV) have never been isolated, strongly suggesting that k_2 is very much greater than k_1 . Even if the first step is reversible the overall rate should bear a close relationship to k_1 . A more complex situation holds for thallium(III). Since $C_6H_{13}\cdot CH(OMe)\cdot CH_2Tl(OAc)_2$ could be isolated, k_2 cannot be significantly greater than k_1 . In fact, it is probably much less: thallium(III) acetate is not very soluble in

organothallium compounds isolated from the reaction of thallium(III) acetate with olefins in alcoholic solvents have all possessed two acetoxy-substituents on the metal atom,^{3,22} it would appear that thallium resembles mercury more closely than it does lead and that ligand exchange is not important for this metal either. We have, then, a phenomenon which is confined to lead(IV). The effect of the addition of methanol in small quantities to this oxidant is greatly to increase the rate of its electrophilic attack on styrene.¹⁰ It is highly probable, then, that the reaction time quoted for lead tetraacetate in Table 1 is abnormally short and is not comparable with the other two values.

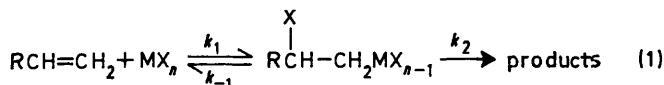
TABLE 1

The oxidation of oct-1-ene (0.01 mol) by lead(IV), thallium(III), and mercury(II) acetates (0.01 mol) in methanol (10 ml) at 60°

Oxidant	Reaction time (h)	Residual olefin (%)	Products (%)					
			(1)	(2)	(3) ^b	(4)	(5) ^c	(6)
Pb ^{IV}	0.75	3	23	52	12	1.5	5	
Tl ^{III}	12	2	6	10	55	23	Trace	
Hg ^{II} ^a	0.15	2						90

^a Analysis after reduction of the crude product with sodium borohydride. ^b No authentic sample available; correction factor assumed identical to (4). ^c No authentic sample available; yield estimated.

methanol, yet on addition of olefin the solution became homogeneous within 0.25 h, leaving very little olefin but producing essentially no volatile products. It is likely, too, that adduct formation is reversible since a positive test for thallium(III) was still given by the solution until product formation was complete.*



Secondly, ligand exchange does not proceed at the same rate for the three oxidants. Lead(IV) undergoes this process very rapidly with nucleophilic solvents^{14,18} whereas mercury(II) acetate appears not to exchange at a detectable rate. All organomercurials obtained by the reaction of mercury(II) acetate with olefins or arenes still retain an acetate group on the mercury atom, irrespective of the solvent employed.^{3,6,19-21} Now, as the few

* Ouellette has reached a similar conclusion in a study of the oxidation of cyclopropanes in acetic acid.¹⁵ More recent results suggest the relative electrophilicities of the three oxidants to be $Tl^{III} > Hg^{II} > Pb^{IV}$.¹⁶ Whether data obtained for cyclopropanes in acetic acid are applicable to the oxidation of olefins in methanol is a moot point. In particular, the earlier work with thallium was complicated by the formation of a double salt of thallium(III) and thallium(I), no account was taken of whether adduct formation might be reversible (such a step is compatible with the strange kinetic behaviour observed), and the possibility that the adduct itself might generate iodine on treatment with potassium iodide was not excluded (*cf.* the behaviour of arylthallium bistrifluoroacetates¹⁷). As we argue later it is also likely that the rate of decomposition of the adduct relative to that of its formation is much enhanced when acetic acid is the solvent.

¹⁵ R. J. Ouellette, A. South, and D. L. Shaw, *J. Amer. Chem. Soc.*, 1965, **87**, 2602.

¹⁶ R. J. Ouellette, R. D. Robins, and A. South, *J. Amer. Chem. Soc.*, 1968, **90**, 1619; A. South and R. J. Ouellette, *ibid.*, p. 7064; R. J. Ouellette, D. Miller, A. South, and R. D. Robins, *ibid.*, 1969, **91**, 971.

Turning next to the products of reaction, the mercury(II) oxidation presents the simplest case. After reduction of the organomercurial adduct the only product detected, other than a trace of residual olefin, was 2-methoxyoctane; neither 1-methylheptyl acetate from reduction of $C_6H_{13}\cdot CH(OAc)\cdot CH_2HgOAc$ nor octan-2-ol which can also be produced from this adduct,⁸ could be detected. We conclude, therefore, that the solvent reacts exclusively at the β -carbon atom of the cationic intermediate resulting from electrophilic attack by mercury(II) acetate on the olefin (Scheme 2), be this the symmetrical mercurinium ion favoured by most workers^{6,23,24} or an unsymmetrical carbonium-like ion.²⁵ In the absence of ligand exchange on the mercury atom, concerted addition to the double bond can be ruled out

¹⁷ A. McKillop, J. D. Hunt, M. J. Zelesko, J. S. Fowler, E. C. Taylor, G. McGillivray, and F. Kienzle, *J. Amer. Chem. Soc.*, 1971, **93**, 4841.

¹⁸ J. K. Kochi, *J. Amer. Chem. Soc.*, 1965, **87**, 1811, 2500, 3609; J. K. Kochi, J. D. Bacha, and T. W. Bethea, *ibid.*, 1967, **89**, 6538; R. O. C. Norman, C. B. Thomas, and J. S. Willson, *J. Chem. Soc. (B)*, 1971, 518; *J.C.S. Perkin I*, 1973, 325; D. de Vos, J. Wolters, and A. van der Gen, *Rec. Trav. chim.*, 1973, **92**, 701 and references therein; M. Lj. Mihailovic and R. E. Partch, in ref. 1b, p. 97.

¹⁹ H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, 1969, **91**, 5646.

²⁰ F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, 1966, **88**, 993; H. C. Brown and J. T. Kurek, *ibid.*, 1969, **91**, 5647; H. C. Brown and P. J. Geoghegan, *J. Org. Chem.*, 1970, **35**, 1844; D. H. Ballard and A. J. Bloodworth, *J. Chem. Soc. (C)*, 1971, 945; J. J. Perie, J. P. Laval, J. Roussel, and A. Lattes, *Tetrahedron*, 1972, **28**, 675.

²¹ A. Lethbridge, unpublished results.

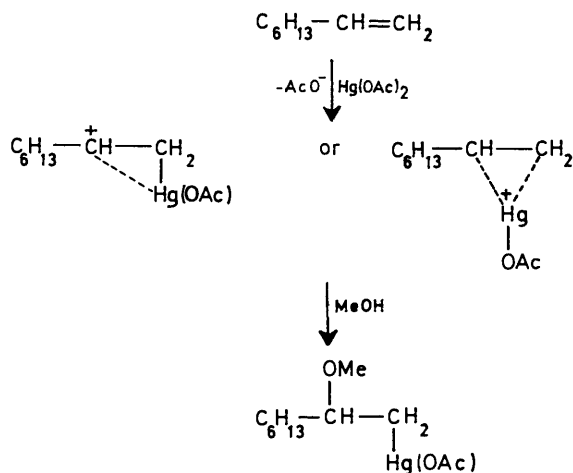
²² S. Uemura, K. Zushi, M. Okano, and K. Ichikawa, *J.C.S. Chem. Comm.*, 1972, 234.

²³ G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, 1973, **95**, 6067.

²⁴ R. D. Bach and R. F. Richter, *J. Amer. Chem. Soc.*, 1972, **94**, 4747.

²⁵ P. B. D. de la Mare and R. Bolton, 'Electrophilic Addition to Unsaturated Systems,' Elsevier, Amsterdam, 1966, p. 113.

as it must result in introduction of a β -acetoxy-substituent. Recent work on the stereochemistry of

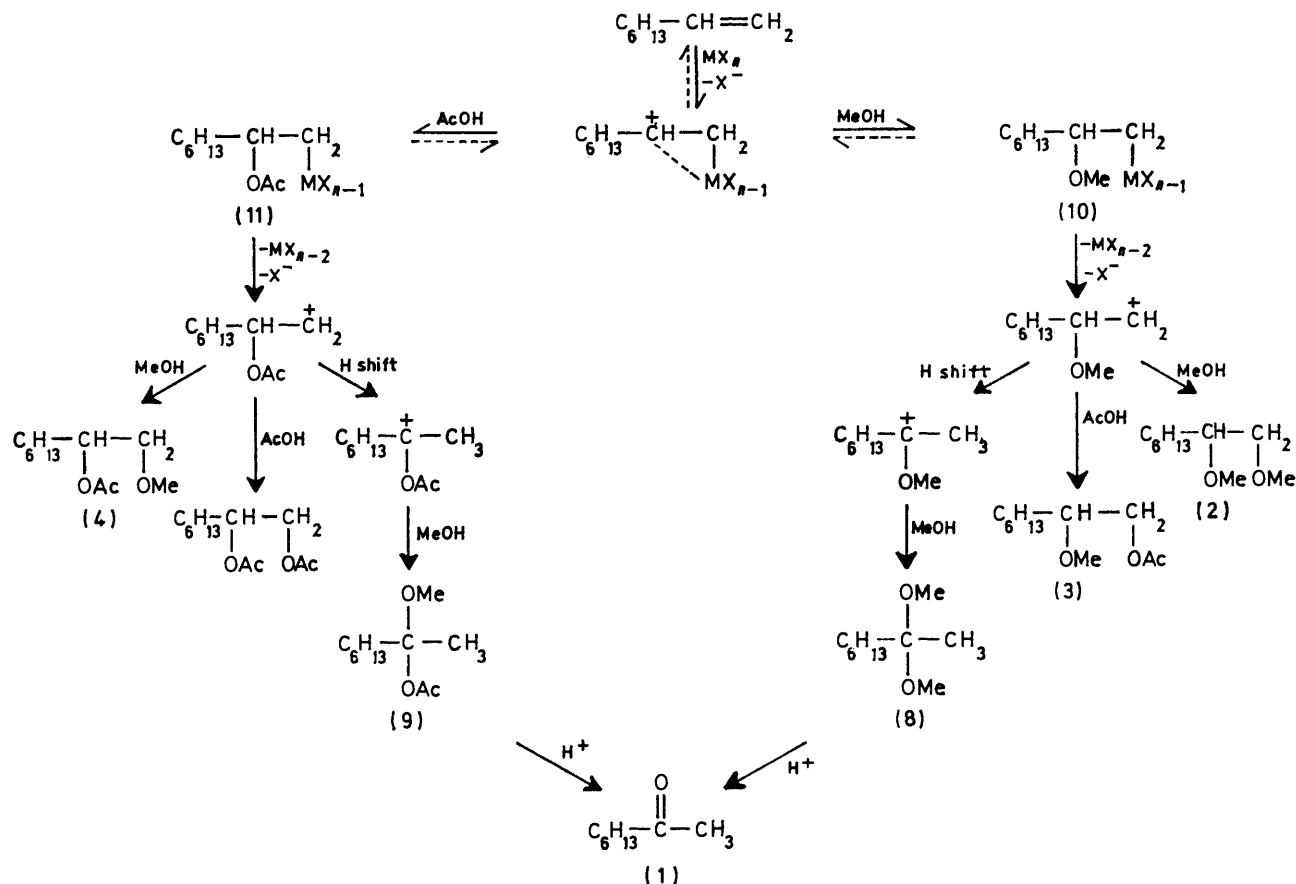


SCHEME 2

addition of mercury(II) salts to alicyclic olefins supports this view.^{24,26}

position modes of the respective adducts must also be considered. Scheme 3 sets out the routes by which the observed products might arise, it being assumed, for the sake of simplicity, that 'free' carbonium ions are involved at each of the two stages of reaction. That the acetal (8) was the precursor of octan-2-one⁷ was demonstrated by injecting the product before work-up into a gas chromatograph. In both cases (8) was present in much greater quantities than the ketone whereas, after work-up, the yield of ketone had increased substantially and the acetal was completely absent. Although no authentic (9) was available, experience in this laboratory has shown that geminal disubstituted compounds of this kind have shorter retention times on g.l.c. than their vicinal isomers. In no experiment did extra peaks occur in this region of the trace.

In the first stage of the reaction, the formation of the adduct, lead again appears to be intermediate in behaviour between mercury and thallium. We noted above that adduct formation with mercury(II) involved exclusive attack by methanol on the β -carbon atom. Likewise, an insignificant fraction of the products from



SCHEME 3 M = Tl or Pb; X = MeO or AcO; n = 3 or 4

Disentangling the mechanisms of the thallium(III) and lead(IV) oxidations is more difficult since the decom-

²⁶ W. L. Waters, T. G. Traylor, and A. Factor, *J. Org. Chem.*, 1973, **38**, 2306.

lead(IV) oxidation bear an acetate group on this atom and yet a sizeable yield of (4) is obtained with thallium(III). We considered three possible explanations for this.

(i) Concerted addition occurs to an increasing extent

across the series $\text{Hg}(\text{OAc})_2$, $\text{Tl}(\text{OAc})_3$, $\text{Pb}(\text{OAc})_4$. Concerted addition of mercury(II) acetate across the double bond does not occur (see above) and lead(IV) undergoes rapid ligand exchange with the result that, in methanol, the lead(IV) oxidant is a mixture of five species. We know nothing about the relative concentrations of these but, since ligand exchange is rapid, there are *ca.* 10 times as many potential methoxy-ligands as acetoxy, and the replacement of acetoxy by methoxy increases the electrophilicity of the lead(IV),¹⁰ it is probable that the active lead(IV) electrophiles possess a high proportion of methoxy-ligands. Concerted addition with incorporation of a β -acetoxy-substituent might thus be a rare process.* Thallium(III), however, is not amenable to ligand exchange and it may be that this is the only one of the oxidants able to undergo concerted addition to any extent.

(ii) The ratio of β -acetoxy- to β -methoxy-substituted products is not dependent on the relative rates of attack of acetate (or acetic acid) and methanol on the 'thallium ion.' Formation of the thallium adduct is readily reversible so that, if the adduct (10; $\text{M} = \text{Tl}$, $\text{X} = \text{OAc}$, $n = 3$) were less stable than (11; $\text{M} = \text{Tl}$, $\text{X} = \text{OAc}$, $n = 3$) or the rate of decomposition of (11) were the greater,[†] then a disproportionately high percentage of β -acetoxy-products would be formed. The adduct-forming step is irreversible with mercury(II) acetate, and with lead(IV) the very fast decomposition of the adducts could prevent significant equilibration of (10; $\text{M} = \text{Pb}$, $n = 4$) and (11; $\text{M} = \text{Pb}$, $n = 4$).

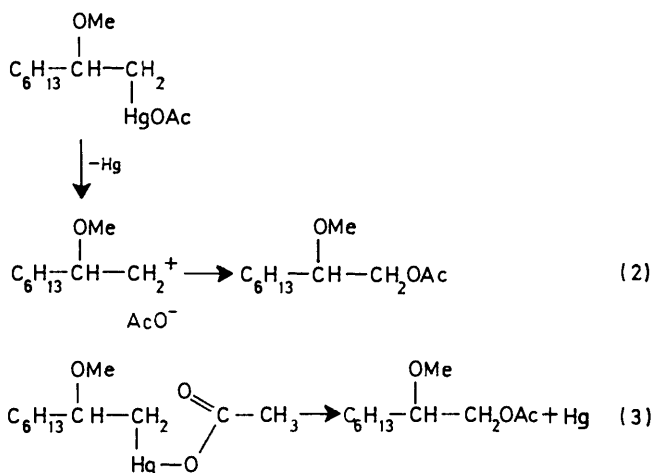
(iii) The position of substituents in the final products does not reflect their position in the preceding adduct. Such would be the case if either an acetoxy- or a methoxy-group migrated during the decomposition step. Evidence that this is so is discussed subsequently.

Let us consider next the decomposition step. Once again mercury(II) offers the simplest situation though, since substantially more severe conditions were required to bring about any decomposition and even then only 2% of products could be obtained, the results should be treated with some caution. The only product observed was (3). Now there is at least 40 times more methanol in the system than acetic acid and, moreover, the latter is the worse nucleophile. It cannot then be that the mercury group is displaced exclusively by acetic acid in an $\text{S}_{\text{N}}1$ or an $\text{S}_{\text{N}}2$ process. The alternative is that the acetoxy-ligand on the mercury atom in (7) ends up on the terminal carbon atom either *via* an ion-pair [reaction (2)] or by a concerted $\text{S}_{\text{N}}i$ process [reaction (3)]. In so far as a discrete ion pair would be expected to undergo at least some collapse with incorporation of solvent to give (2), we favour the latter possibility.

Decomposition of the adducts (10) from thallium and lead appears to lead to three products: octan-2-one,

* Results claimed to demonstrate concerted addition of lead(IV) acetate to acenaphthylene in methanol²⁷ are, at least, equally consistent with other interpretations and, in any case, data obtained on a rigid, disubstituted aromatic olefin are unlikely to be a useful guide to the behaviour of a monosubstituted aliphatic olefin.

1,2-dimethoxyoctane, and the mixed methoxy-acetoxy compound (3). It is possible that some of the ketone originates from (9) rather than (8) in which case its precursor could also be the acetoxy-containing adduct (11), but our inability to detect (9) before work-up makes this unlikely. Formation of (3) is more important with thallium than with lead, as would be expected if uptake of an acetoxy-group on C-1 were to occur solely *via* an



$\text{S}_{\text{N}}i$ process analogous to reaction (3). Ligand exchange on the lead atom would ensure that there are few acetate ligands available to undergo this reaction.

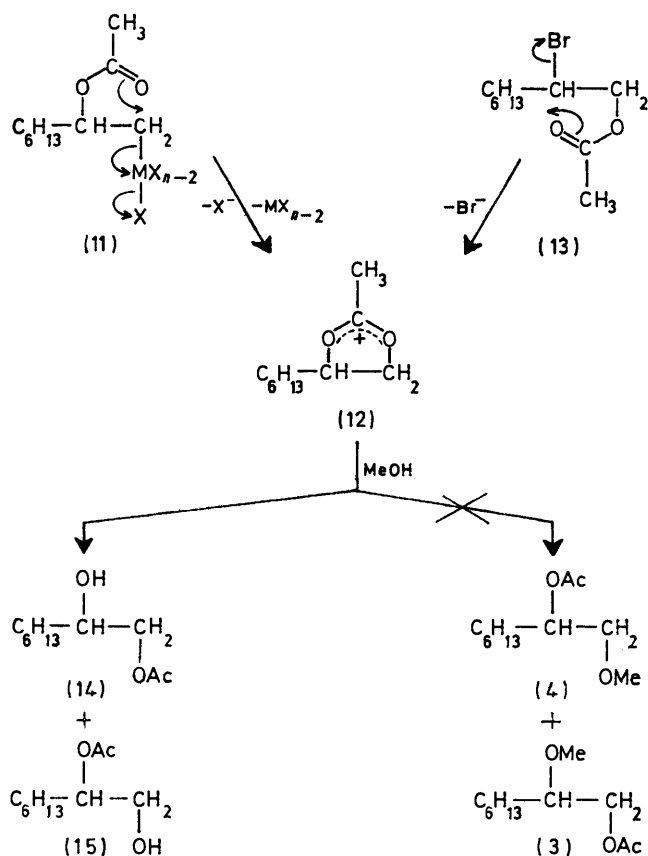
It is tempting to assign formation of the remaining product (4) to uptake of solvent on heterolysis of the carbon-metal bond in adduct (11). Whilst such an explanation might be acceptable in the case of the lead(IV) oxidation when the yield of (4) is very low, it poses problems in the thallium(III) oxidation. In particular, why do hydride shift and $\text{S}_{\text{N}}i$ displacement by acetate not compete with nucleophilic attack of solvent during decomposition of the adduct? The absence of an authentic sample of (9) makes it uncertain whether hydride shift is, in fact, absent. Certainly it should be less easy from (11) than from (10) since a methoxy-substituent is the better group at stabilising the resultant carbonium ion centre. However, there is no reason to suppose that an $\text{S}_{\text{N}}i$ decomposition would be any more difficult, yet with neither oxidant is any octane-1,2-diol diacetate produced.

The possibility must be considered then that the positions of substituents in the product do not reflect their positions in the intermediate adduct. This could most readily arise if heterolysis of the carbon-metal

[†] Circumstantial evidence that the decomposition rate of (11; $\text{M} = \text{Tl}$, $\text{X} = \text{OAc}$, $n = 3$) is faster than (10; $\text{M} = \text{Tl}$, $\text{X} = \text{OAc}$, $n = 3$) is that almost all the thallium adducts reported have possessed β -alkoxy-substituents.^{3,22} An explanation of an enhanced rate for (11) could be that a neighbouring acetoxy-group assists heterolysis of the carbon-thallium bond. This would result in an acetoxonium ion but, as we show later, there is evidence against this species being formed in this system. It may be significant that the two characterised organothallium adducts possessing β -acetoxy-substituents have both had these rigidly oriented in such a way as to preclude neighbouring-group participation.⁵

²⁷ B. Rindone and C. Scolastico, *Tetrahedron Letters*, 1973, 1479.

bond were to occur with neighbouring-group assistance from the β -acetoxy-substituent²⁸ and the resultant acetoxonium ion were converted into (3) and (4) through nucleophilic attack by the solvent. To test this, a solution of 2-bromo-octyl acetate (13) in dry methanol was stirred with silver acetate at 60° until precipitation of silver bromide was complete. Analysis of the product showed (3) and (4) to be absent, the sole product being a mixture, inseparable by g.l.c., of the isomeric hydroxy-acetates (14) and (15). We have shown previously that, despite all attempts to use dry solvents, enough adventitious water is taken up by hygroscopic ones to quench any acetoxonium ion generated.^{8,11} It would appear that the vast excess of methanol is unable to compete with the extremely rapid attack by water. Now the same 'dry' methanol employed in this solvolysis had been used in the oxidation reactions and, since no hydroxy-acetates could be detected in these cases,



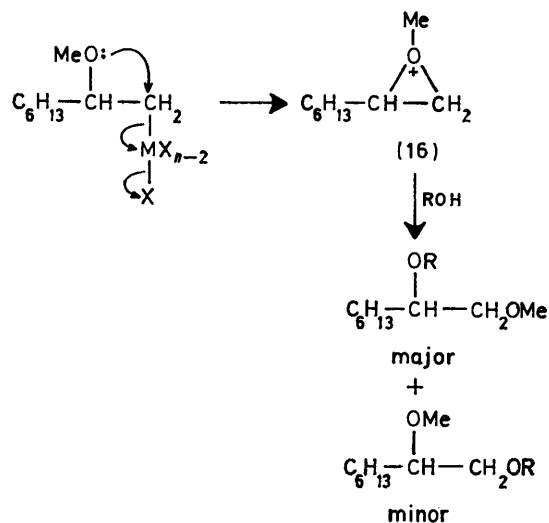
acetoxonium ions cannot have been generated during oxidation.* It seems unlikely, then, that an acetoxy-group is ever present on C-2.

The only other means by which substituent scrambling could occur would be if a methoxy-group were to

* Lead(IV) acetate leaves hydroxy-acetates largely unchanged¹¹ and there is no evidence that thallium(III) acetate will oxidise alcohols.

²⁸ C. U. Pitman, S. P. McManus, and J. W. Larsen, *Chem. Rev.*, 1972, **72**, 357.

migrate (Scheme 5). In similar rearrangements of β -methoxy-substituents²⁹ the major product arises by nucleophilic attack on the more highly substituted



carbon atom of an ion such as (16), in contrast to the acid-catalysed ring opening of epoxides when reaction at the opposite carbon atom usually predominates.³⁰ However, acetic acid or free acetate anion would stand little chance of quenching the cyclic oxonium ion (16) in competition with methanol, so that the major product should be (2). The only way (16) could lead to good yields of (3) and (4) would seem to be if heterolysis of the carbon-metal bond occurred with formation of an ion-pair, the counter-ion being an acetate anion. Such ion-pairs have been postulated in the solvolyses of 5- and 6-methoxyalkyl bromobenzenesulphonates³¹ and the counter-ion could be expected to be acetate only in the decomposition of the thallium adduct, hence the high yield of (4) only from this oxidation.

The ultimate test of methoxy-migration is to show that (4) results from the decomposition of $C_6H_{13}CH(OMe)CH_2Tl(OAc)_2$ under the reaction conditions. This we attempted to do but difficulties in handling this labile compound prevented its complete characterisation, so that the results must be treated with a degree of circumspection. Addition of oct-1-ene in methanol to thallium(III) acetate in methanol, followed by solvent removal after 15 min and repeated trituration with light petroleum, left a viscous oil. The ¹H n.m.r. spectrum of this was fully consistent with its being the adduct (10; M = Tl, X = OAc, n = 3); in particular, the absence of any signal centred at *ca.* τ 5.0 rules out the presence of a product possessing an acetoxy-group on the β -carbon atom (see Experimental section for comparative spectra). The oil was

²⁹ S. Winstein and L. L. Ingraham, *J. Amer. Chem. Soc.*, 1952, **74**, 1160; S. Winstein, C. R. Lindgren, and L. L. Ingraham, *ibid.*, 1953, **75**, 155.

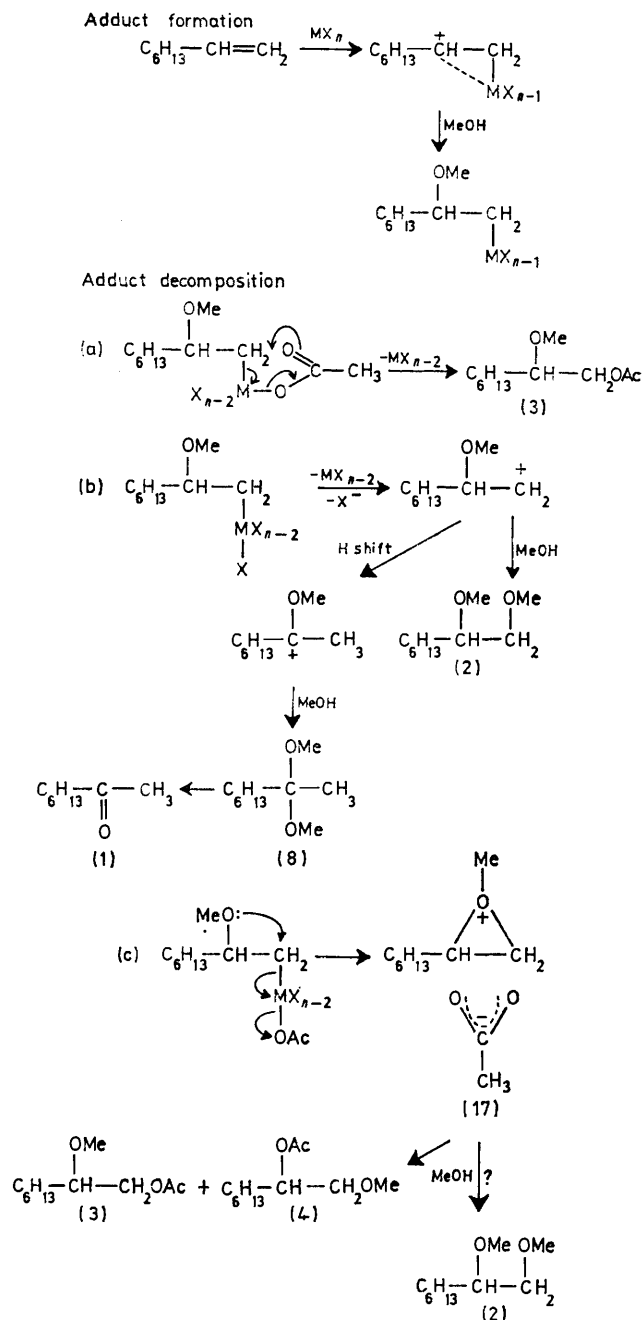
³⁰ R. E. Parker and N. S. Isaacs, *Chem. Rev.*, 1959, **59**, 737; J. K. Addy and R. E. Parker, *J. Chem. Soc.*, 1963, 915.

³¹ E. L. Allred and S. Winstein, *J. Amer. Chem. Soc.*, 1967, **89**, 3998, 4012.

heated in methanol at 60° for 12 h. After work-up, both (3) (30%) and (4) (19%) were present together with small amounts of (1) and (2). Such a high yield of a

in place before decomposition, so that (4) must have arisen from methoxy-group migration.

We believe then that oxidation of oct-1-ene by the three metal acetates is best summarised by Scheme 6. Adduct formation occurs with exclusive uptake of methanol on the β -carbon atom. In the case of mercury and thallium the ligands on the metal are acetoxy but with lead they may also be methoxy. Decomposition of the adduct can occur in three ways. (a) An S_Ni displacement of the metal substituent leads to incorporation on C-1 of an acetate ligand from the metal. This is the exclusive mode of decomposition of the mercury adduct and the principal one for the thallium adduct, but it is of only minor importance for lead, partly because of the reduced likelihood of there being acetate groups on this metal. (b) Heterolysis of the carbon-metal bond leads to formation of a carbonium ion, or an incipient carbonium ion, which reacts in one of two ways: attack by the solvent gives (2), whereas hydride shift leads to the acetal and ultimately octan-2-one. This unassisted heterolysis is most marked in the lead(IV) oxidation, since the leaving group ability of a metal substituent falls in the order $Pb > Tl > Hg$.² (c) Anchimeric assistance to heterolysis by the β -methoxy-substituent produces an ion-pair (17) which collapses principally to (4) but also to (3) and possibly to (2). This is a major process for the thallium adduct, though its importance in the lead(IV) reaction may be masked by the lack of acetate ligands on the adduct from this oxidant.



SCHEME 6 M = Hg, Tl, or Pb; X = MeO or AcO; $n = 2-4$.

β -acetoxy-product would have been apparent in the n.m.r. spectrum of the adduct had this substituent been

* The three ions of highest mass, m/e 201, 159, and 147, arise by loss of the three substituents on C-2 (OMe, CH_2OAc , and C_6H_{13} respectively), the last two, in which both methoxy-groups remain to stabilise the positive charge, being much more abundant than the first. The other major ions are derived from these primary fragments.

To test whether (1) and (2) were formed competitively from the same incipient carbonium ion, we oxidised the olefin with lead(IV) in the presence of reduced amounts of methanol, which should result in enhanced yields of (1) relative to (2). These experiments were conducted at the same concentration and temperature as those in Table 1 but ethylene dichloride containing known amounts of methanol was employed as solvent. The results are set out in Table 2 together with the comparable experiment from Table 1. Reaction time was substantially longer than in pure methanol, in keeping with the less polar nature of the solvent and the reduced electrophilicity of the lead(IV) through a shift of the ligand-exchange equilibria. One major new product was detected and identified as the acetal (18) on the basis of its mass spectrum,* all attempts to prepare an authentic sample by a route analogous to that used in the synthesis of (8) having failed. The compound, surprisingly, survived work-up, suggesting it is more resistant to hydrolysis than (8). In addition three other products were detected in trace amounts (<0.2%), namely the hydroxy-acetates (14) and (15) and the acetoxy-ketone (19).

The two potential routes to (18) are shown in Scheme 7. The second of these would have disturbing implications if dimethyl acetals are in equilibrium with their parent ketones under the reaction conditions, since our earlier conclusion that (9) is not formed might then be invalid. However, when we subjected 1-acetoxyoctan-2-one to

the reaction conditions we could never detect any (18) and conclude that acetals cannot be regenerated in this way. We are left then with the alternative, the oxidation of 2-methoxyoct-1-ene. This compound could not be detected either before or after work-up, but that is not surprising since it should be much more susceptible to electrophilic attack than oct-1-ene. The one drawback to this hypothesis is the difficulty of explaining why, in (18), only acetate is incorporated on C-1. There

(c) of Scheme 6, involving less localisation of charge, would be favoured over step (b).

EXPERIMENTAL

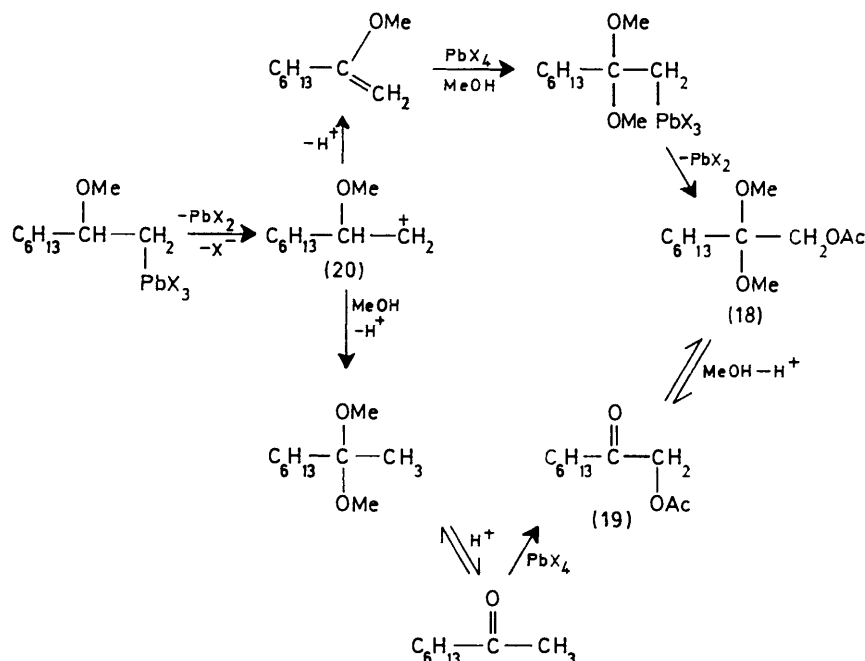
The analytical techniques and a number of the compounds employed in this study have been described previously.^{8,10,11,13} Methanol was dried by refluxing over calcium oxide, the distillate being stored over molecular sieve (4 A) until use.

TABLE 2

The oxidation of oct-1-ene (0.01 mol) by lead(IV) acetate (0.01 mol) at 60° in ethylene dichloride containing methanol (total volume 10 ml)

Vol of MeOH (ml)	Reaction time (h)	Residual olefin (%)	Products (%)					
			(1)	(2)	(3) ^b	(4)	(5) ^b	(18) ^b
10 ^a	0.75	3	23	52	12	1.5	5	
1.2	10	1	10	23	34	26	1	6.2
0.6	16	1	8.2	16	35	28	1.5	8.4

^a Results from Table 1. ^b See footnotes b and c in Table 1.



was no evidence for the formation of 1,2,2-trimethoxyoctane or even 1-methoxyoctan-2-one. In the corresponding experiment in Table 1 no (18) was found, suggesting that 2-methoxyoct-1-ene is not formed when methanol is used as solvent.

Returning to the main reason for carrying out oxidations in the mixed solvent system, it can be seen that reducing the amount of available methanol not only significantly reduces the yield of (2) but also causes that of octan-2-one to fall. However, the ratio of nucleophilic attack by methanol to hydrogen rearrangement falls from 1 : 1.9 to 1 : 2.3, in line with expectation. The yield of products derived from the carbonium ion (20) falls from a maximum of 75 to ca. 24%, as expected from the decrease in the solvent polarity; steps (a) and

Other Materials.—1,2-Dimethoxyoctane. A solution of octane-1,2-diol⁸ (5 g) in 4M-sodium hydroxide (50 ml) and dimethyl sulphate (15 g) was heated at the reflux temperature for 2 h, cooled, poured into water, and extracted with ether. G.l.c. analysis of the product remaining after removal of the solvent showed there to be present both the dimethyl ether and the two monomethyl ethers. Preparative g.l.c. on a 10% polyethylene glycol adipate column, followed by distillation, gave 1,2-dimethoxyoctane (0.7 g, 12%) as a liquid, b.p. 80° at 20 mmHg; τ 6.61, 6.64 (2s, OMe), and 6.63 (2m, CHCH₂) (total 9H); 8.25—9.25 (13H, aliphatic envelope), *m/e* 174 (0.2%, M⁺), 129 (65, C₆H₁₃CH=O⁺Me), 128 (10, M - C₂H₆O), 97 (67, 129 - MeOH), 71 (16, 129 - C₄H₁₀), 69 (18, 97 - C₂H₄), 55 (100, 97 - C₃H₆), and 45 (68, CH₂=O⁺Me), *m** 94.2 (174 → 128),

72.9 (129 \rightarrow 97), 49.1 (97 \rightarrow 69), 39.1 (129 \rightarrow 71), and 31.2 (97 \rightarrow 55).

2,2-Dimethoxyoctane. Trimethyl orthoformate³² (1.5 g), octan-2-one (1.3 g), and dry hydrogen chloride (100 mg) in methanol (7 ml) were allowed to stand for 24 h. Excess of sodium methoxide was added, the solvent was removed, and the residue was distilled to give 2,2-dimethoxyoctane (0.8 g, 45%) as a liquid, b.p. 65–70° at 12 mmHg; τ 6.85 (6H, s, OMe) and 8.27–9.20 (16H, aliphatic envelope); *m/e* 159 (3%, *M* – Me), 143 (27, *M* – MeO), 142 (17, *M* – MeOH), 127 (2, *M* – Me – MeOH), 99 (6), 89 (59, *M* – C₆H₁₃), 85 (100), 72 (77), and 55 (33), *m** 35.6 (85 \rightarrow 55).

1-Methoxymethylheptyl acetate. 1-Methoxyoctan-2-ol was prepared by a modification of the method of Reeve and Sadle.³³ 1,2-Epoxyoctane (4.3 g) and methanol (1.5 ml) containing dissolved sodium (0.1 g) were heated on a steam bath for 3 h. After cooling, the mixture was fractionated to give 1-methoxyoctan-2-ol (4.6 g, 85%) as a liquid, b.p. 88° at 15 mmHg; τ 6.2–7.0 (complex m, CHCH₂) and 6.61 (s, OMe) (total 6H), 7.25br (1H, s, exchangeable in D₂O, OH), and 8.3–9.4 (13H, aliphatic envelope), *m/e* 115 (22%, C₆H₁₃CH=OH⁺), 114 (14, *M* – C₂H₆O), 97 (61, C₇H₁₃⁺), 75 (11, HO=CHCH₂OMe⁺), 69 (18, C₅H₉⁺), 55 (100, C₄H₇⁺), 47 (17), 45 (29, CH₂=OMe⁺), 43 (28), and 41 (24); *m/e* 129 (loss of \cdot CH₂OH from isomeric 2-methoxyoctan-1-ol) was negligible. The alcohol (4 g) was heated at reflux with acetic anhydride (10 ml) and sodium carbonate (1 g) for 1 h and the cooled product was poured into water. The ether extracts, after washing with sodium carbonate solution, were dried (MgSO₄), the solvent removed, and the residue distilled to give 1-methoxymethylheptyl acetate (4.2 g, 83%) as a liquid, b.p. 100–102° at 15 mmHg, τ 4.97br (1H, quintet, CH), 6.56 (d, *J* 5.5 Hz, CH₂O) and 6.63 (s, OMe) (total 5H), 7.93 (3H, s, OAc), and 8.2–9.35 (13H, aliphatic envelope) (Found: C, 65.0; H, 10.6. C₁₁H₂₂O₃ requires C, 65.3; H, 10.9%).

2-Bromo-octyl acetate. An ethereal solution of bromine (0.1 mol) was added dropwise to a cooled, stirred solution of octanal (0.1 mol) in ether (100 ml) over 1 h. After being washed with sodium hydrogen carbonate solution and dried (MgSO₄), the solvent was removed and the residue distilled to give α -bromo-octanal (14 g, 88%) as a liquid, b.p. 50° at 0.4 mmHg (lit.,³⁴ 110–111° at 23 mmHg), τ 0.75 (1H, d, *J* 3.3 Hz, CHO), 5.77 (1H, t of d, *J* 3.3, *J'* 7.0 Hz, CHBr), and 7.75–9.4 (13H, aliphatic envelope). An ice-cold, weakly alkaline solution of sodium borohydride was added dropwise with stirring to a cooled solution of the bromo-aldehyde (10 g) in methanol (25 ml). After a further 0.5 h stirring, the solution was poured into water, extracted with ether, and the extract was dried (MgSO₄). Evaporation of the ether left crude 2-bromo-octan-1-ol, τ 5.64–6.70 (3H, complex m, CHCH₂), 7.55br (1H, s, exchangeable in D₂O, OH), and 7.9–9.4 (13H, aliphatic envelope). The crude bromohydrin (7 g) and *NN*-dimethylaniline (8 g) were dissolved in dry ether (30 ml) and acetyl bromide (12 ml)

* The mixture gives a homogeneous peak on g.l.c. and the two compounds are probably in dynamic equilibrium (*cf.* ref. 35). The mass spectrum of this g.l.c. peak shows fragments assignable to both isomers: *m/e* 157 (loss of HOCH₂ from the 2-acetate) and *m/e* 115 (loss of AcOCH₂ from the 1-acetate).

³² H. A. Weidlich and W. Schulz, W. Ger. P. 919,465 (*Chem. Abs.*, 1958, **52**, 14,685e).

³³ W. Reeve and A. Sadle, *J. Amer. Chem. Soc.*, 1950, **72**, 1251.

³⁴ L. A. Yanovskaya and A. P. Terent'ev, *Zhur. obshchei Khim.*, 1952, **22**, 1598.

was added dropwise with cooling and stirring. The mixture was then refluxed for 2 h, cooled, and poured into water. The ether extracts were washed with dilute sulphuric acid and sodium hydrogen carbonate solution and dried (MgSO₄). Removal of the solvent left a viscous oil which, upon distillation, yielded 2-bromo-octyl acetate (7.2 g, 79%) as an oil, b.p. 80° at 0.4 mmHg, τ 5.60–6.05 (3H, m, CHCH₂), 7.91 (3H, s, OAc), and 7.9–9.4 (13H, aliphatic envelope) (Found: C, 47.4; H, 7.5. C₁₀H₁₉BrO₂ requires C, 47.8; H, 7.6%).

Octane-1,2-diol monoacetate. 1,2-Epoxyoctane (4 g) was heated in acetic acid (10 ml) at 60° for 48 h. Fractionation of the residue gave a mixture of the 1- and 2-acetates of octane-1,2-diol* (4.3 g, 73%) as a colourless liquid, b.p. 142° at 15 mmHg (lit.,³⁶ 77° at 0.4 mmHg), τ 4.8–5.4 (m, probably CH of 2-acetate) and 5.7–6.5 (m, CHCH₂ of 1-acetate and CH₂ of 2-acetate) (total 3H), 7.33 (1H, s, exchangeable in D₂O, OH), 7.94 (3H, s, OAc), and 8.2–9.35 (13H, aliphatic envelope).

Octane-1,2-diol diacetate. Octane-1,2-diol (8 g) and anhydrous sodium acetate (6 g) in acetic anhydride (20 ml) were heated under reflux for 1 h. After cooling, water was added and the product was extracted with ether. The extracts were washed with sodium hydrogen carbonate solution and dried (MgSO₄). Evaporation of the solvent and distillation of the residue gave octane-1,2-diol diacetate (11 g, 91%) as a viscous oil, b.p. 114° at 4 mmHg (lit.,³⁷ 110–113° at 6 mmHg), τ 4.80–5.16 (1H, m, CH), 5.83 and 5.92 (2H, 2d of d, *J* 4.0, *J'* 6.5, *J''* 11.5 Hz, non-equiv. CH₂), 7.97 (6H, s, OAc), and 8.2–9.4 (13H, aliphatic envelope).

1-Acetoxyoctan-2-one was prepared by the method of Sung Moon and Bohm³⁸ and purified by preparative gas chromatography. It had m.p. 40.5–42° (lit.,³⁸ 41–42°); n.m.r. spectrum as reported earlier except that the C-1 singlet was at τ 5.52.

Oxidations.—The general procedure was as follows: oct-1-ene (0.01 mol) in dry methanol (5 ml) was added to a solution of the metal oxidant (0.01 mol) in methanol (5 ml) and the mixture was heated at 60° until tests showed that all the oxidant had been consumed. These tests were: for lead(IV), the absence of a chocolate-coloured precipitate of lead dioxide on adding a drop of the solution to water; for thallium(III) and mercury(II), the absence of a brown or a yellow precipitate, respectively, when a drop of the solution was added to dilute alkali. The products of the lead(IV) and thallium(III) oxidations were poured into water, the solution was extracted with ether, and the extracts were washed with saturated sodium hydrogen carbonate solution and dried (MgSO₄). The solvent was evaporated and the product analysed by g.l.c. In both instances a product was obtained with a similar retention time to 1-methoxymethylheptyl acetate which was identified as the isomeric 2-methoxyoctyl acetate on the basis of its mass spectrum, *m/e* 142 (5%, *M* – AcOH), 129 (100, C₆H₁₃CH=OMe⁺), 117 (9, MeO=CHCH₂OAc⁺), 97 (37, C₇H₁₃⁺), 85 (5, 117 – MeOH), 69 (11, C₅H₉⁺), 55 (51, C₄H₇⁺), 45 (30), and 43 (45, CH₃C=O⁺),

³⁵ T. Cohen, M. Dughi, V. A. Notaro, and G. Pinkus, *J. Org. Chem.*, 1962, **27**, 814; H. P. Kaufmann and R. Schickel, *Fette Seifen Anstrichmittel*, 1964, **66**, 21 (*Chem. Abs.*, 1964, **60**, 14,412); C. B. Thomas, D.Phil. Thesis, University of York, 1967.

³⁶ W. J. Hickinbottom and D. R. Hogg, *J. Chem. Soc.*, 1954, 4200.

³⁷ L. G. Wolgemuth, U.S.P. 3,403,175 (*Chem. Abs.*, 1969, **70**, 3305).

³⁸ Sung Moon and H. Bohm, *J. Org. Chem.*, 1972, **37**, 4338.

m^* 72.9 (129 \rightarrow 97), 49.1 (97 \rightarrow 69), and 31.2 (97 \rightarrow 55). A minor product had a mass spectrum, m/e 129 (89%, $M - ClCH_2$), 97 (64, $C_7H_{13}^+$), 93/95 (22/8, $M - C_6H_{13}$), 55 (100, $C_4H_7^+$), 45 (89), 43 (56), and 41 (54), and was accordingly identified as 1-chloro-2-methoxyoctane.

In the case of the mercury(II) oxidation the crude mercuriation product was stripped of solvent and reduced by shaking with an aqueous alkaline solution of sodium borohydride for 15 min. Excess of the reductant was destroyed by the addition of dilute hydrochloric acid, the solution was extracted with ether, and the extracts were dried ($MgSO_4$) and, after removal of the solvent, analysed. From the crude product of one preparative scale reaction 1-acetoxymethyl-2-methoxyoctane (90%) was isolated as a grey oil which would not solidify, τ 6.3—6.9br (m, CH) and 6.69 (s, OMe) (total 4H), 7.4—8.0 (2H, m, non-equiv. CH_2), 7.98 (3H, s, OAc), and 8.3—9.3 (13H, aliphatic envelope). The product obtained after borohydride reduction as above gave, on distillation, 2-methoxyoctane (1.1 g, 83%) as a liquid, b.p. 62° at 20 mmHg (lit.,³⁹ 76° at 44 mmHg), τ 6.71 (s, OMe) and 6.6—6.9br (m, CH) (total 4H) and 8.4—9.3 (aliphatic envelope) and 8.88 (d, J 6 Hz, CH_3) (total 16H).

In one experiment employing thallium(III) the solvent was removed after 15 min and the crude product was triturated several times with light petroleum (b.p. 40—60°) to give a viscous oil which decomposed on standing. This was

presumed to be 2-methoxyoctylthallium diacetate, τ 6.62 (m, CH) and 6.65 (s, OMe) (total 4H), 7.97 (d, J 5 Hz, CH_2Tl) and 7.99 (s, OAc) (total 8H), and 8.4—9.4 (13H, aliphatic envelope).

In the experiments set out in Table 2 the methanol was replaced as solvent by the same volume of ethylene dichloride containing a controlled amount of methanol. One of the products obtained under these conditions was identified as 2,2-dimethoxyoctyl acetate on the basis of its mass spectrum, m/e 201 (5%, $C_6H_{13}^+C(OMe)CH_2OAc$), 159 [71, $C_6H_{13}^+C(OMe)_2$], 147 [73, $(MeO)_2C^+CH_2OAc$], 141 (10, 201 — AcOH), 127 (7, 159 — MeOH), 109 (12, 141 — MeOH), 101 (10), 88 [25, $CH_2=C(OMe)_2^{+}$], and 43 (100, $CH_3C\equiv O^+$), m^* 98.9 (201 \rightarrow 141) and 84.2 (141 \rightarrow 109).

Solvolysis.—2-Bromo-octyl acetate (0.001 mol) was heated at 60° in methanol (20 ml) in the presence of silver acetate (0.0015 mol) for 5 h. The solution was then cooled and filtered, the filtrate was poured into water and extracted with ether, and the extract was dried ($MgSO_4$). After removal of the solvent the crude product was analysed by g.l.c.—m.s. and n.m.r. spectrometry.

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³⁹ 'Heilbron's Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.