

Oxidation of Oct-1-ene and *trans*-Oct-4-ene by Lead(IV), Thallium(III), and Mercury(II) Acetates

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The comparative study of the oxidation of oct-1-ene by lead(IV), thallium(III), and mercury(II) acetates in methanol has been extended to other solvents and to the oxidation of an internal olefin, *trans*-oct-4-ene. The general rules developed for the methanol system are found to be applicable to these solvents. In acetic acid, incorporation of an acetoxy-substituent on C-2 of oct-1-ene followed by decomposition of the organometallic adduct *via* an acetoxonium ion gives a high yield of hydroxy-acetates. This yield is boosted in lead(IV) oxidations by the addition of water to the system. The adduct from mercury(II) oxidation is stable but reduction of it with borohydride does not appear to offer a clean means of adding a carboxylic acid across a double bond: substantial reduction of the ester function occurs. There appear to be severe steric constraints to the oxidation of *trans*-oct-4-ene by initial electrophilic addition of the metal acetates but when this does occur there is a stereoselective preference for *anti*-addition. However, the major products are allylic. It is suggested that, in the case of lead(IV) oxidations, these arise by a homolytic process; indeed there is no evidence of heterolytic attack of this oxidant on oct-4-ene.

We recently described a comparative study of the oxidation of oct-1-ene by lead(IV), thallium(III), and mercury(II) acetates in methanol.¹ We concluded that the initial addition to the double bond was not concerted and that there were three ways in which the resultant adduct could decompose, namely, by displacement of the metal substituent by the solvent, incorporation of one of the metal ligands as the carbon-metal bond breaks, or migration of one of the substituents on C-2. We now report an extension of the study to other solvents and to the oxidation of an internal olefin, oct-4-ene.

RESULTS AND DISCUSSION

Oxidation of Oct-1-ene in Acetic Acid.—Acetic acid has frequently been employed as solvent for the oxidation of olefins by lead(IV) acetate. Unfortunately, with the exception of a few olefins which are particularly susceptible to electrophilic attack (*e.g.* ethyl vinyl ether² and α -methylstyrene³), ionic reactions are slow enough for products arising from competitive radical processes to complicate mechanistic studies,³⁻⁵ especially in those cases where a compound may be formed by both path-

ways. On the other hand, as far as is known, oxidations of olefins by thallium(III) or mercury(II) acetate proceed exclusively by ionic mechanisms. We hoped therefore that a comparison of the results obtained with the last two oxidants would enable us to elucidate the mechanisms of electrophilic reactions of lead(IV) acetate with a terminal aliphatic olefin, oct-1-ene being chosen, for reasons described earlier,^{1,6} as representative.

An acetic acid solution of oct-1-ene was heated with lead(IV) acetate at 60° until all the oxidant had been consumed. Five products were identified by comparison with authentic samples. The major one was a hydroxy-acetate [probably a mixture of the isomers (1) and

¹ A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1974, 1929.

² Y. Yukawa and M. Sakai, *Nippon Kagaku Zasshi*, 1966, **87**, 81.

³ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1967, 771.

⁴ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1968, 994.

⁵ E. I. Heiba, R. M. Dessau, and W. J. Koehl, *J. Amer. Chem. Soc.*, 1968, **90**, 2706.

⁶ A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1973, 2763.

(2)^{1,4,7} with minor amounts of the diacetate (3), octan-2-one (4), and the allylic acetates (5) and (6) (unresolved by g.l.c.). A sixth product was tentatively identified as the *gem*-diacetate (7) on the basis of its mass spectrum. Yields are in Table 1 (experiment 1).

The low conversion of oct-1-ene is evidently the result of the competitive destruction of the oxidant in other ways, for example by reaction with the solvent,^{8,9} since substantial amounts of unconverted olefin habitually characterise oxidations in which lead(IV) is only slowly

colouration resulting from hydrolysis of lead(IV) was observed and the yield of products fell.

When thallium(III) was used as oxidant, (1) and (2) were again the major products; in addition, (3), (4), a trace of 1,2-epoxyoctane (8), and an unidentified compound (<2%) were obtained; the total yield was almost quantitative. Increasing the water content of the solvent caused a gradual decrease in the yield of hydroxy-acetate and of diacetate with a concomitant increase in the amount of ketone and octane-1,2-diol (9). There

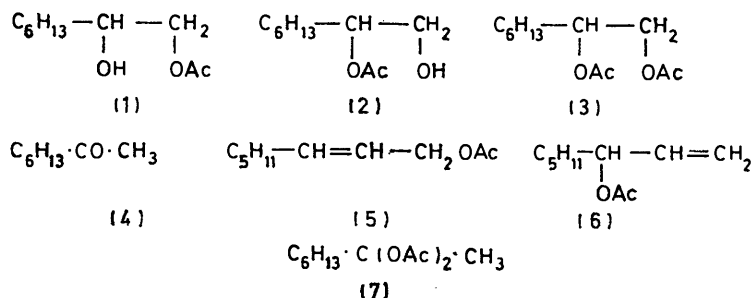


TABLE 1

Products from the oxidation of oct-1-ene (5 mmol) with lead(IV) acetate (5 mmol) in acetic acid (10 ml) at 60°

Expt.	Added H ₂ O (mmol)	Time (h)	Products (%)					
			C ₆ H ₁₃ CH=CH ₂ (1) + (2)	(3)	(4)	(7) ^a	(5) + (6)	
1		8	50	18	2.5	1.0	Trace	1.9
2	5	25	9.5	71	7.3	1.0	1.5	1.5
3	10	22	2.3	80	8.1	1.3	1.0	2.2
4	20	14 ^b	25	65	4.1	2.0	1.0	2.0

^a Approximate yield; no authentic material available. ^b Some hydrolysis of Pb^{IV} occurred during oxidation.

TABLE 2

Products from the oxidation of oct-1-ene (5 mmol) with thallium(III) acetate sesquihydrate (5 mmol) in acetic acid (10 ml) at 60°

Expt.	Added H ₂ O (mmol)	Time (h)	Products (%)					
			C ₆ H ₁₃ CH=CH ₂ (1) + (2)	(3)	(4)	(8)	(9)	
5		12	2	84	7.2	3.8	Trace	
6	5	15	1	86	4.5	6.1	0.1	
7	10	18	1	80	6.1	8.8	Trace	Trace
8	20	16	Trace	77	6.1	13	Trace	2.3
9	100	12	Trace	62	2.9	25	0.3	8.9
10	500	<12	Trace	31	0.7	37	0.5	28

consumed. Rather surprisingly, however, the addition of small amounts of water resulted in no hydrolysis but greatly increased the extent of conversion of the olefin (experiments 2—4). It can be seen, from the time required for destruction of the oxidant, that this is not because the rate of oxidation of the olefin is increased but because the lead(IV) is less rapidly consumed in other ways. Possibly replacement of acetoxy- by hydroxy-ligands on the lead inhibits solvent-induced decomposition of the reagent, be this a radical⁸ or an ionic⁹ process. The limit to the amount of water the oxidant tolerates appears to be about 8% by volume; above this figure (experiment 4) the characteristic brown

is no obvious relationship between the rate of consumption of thallium(III) and the ratio of water to acetic acid.

The results for the major products from both oxidants are in accord with the usual two-stage mechanism.^{1,10} Electrophilic attack by the metal salt followed by nucleophilic attack by the solvent results, in acetic acid containing no added water, in the formation of a labile organometallic adduct (10) bearing an acetoxy-group on C-2. Subsequent heterolysis of the carbon-metal bond occurs preferentially with acetoxy-participation

⁷ T. Cohen, M. Dughi, V. A. Notaro, and G. Pinkus, *J. Org. Chem.*, 1962, **27**, 814.

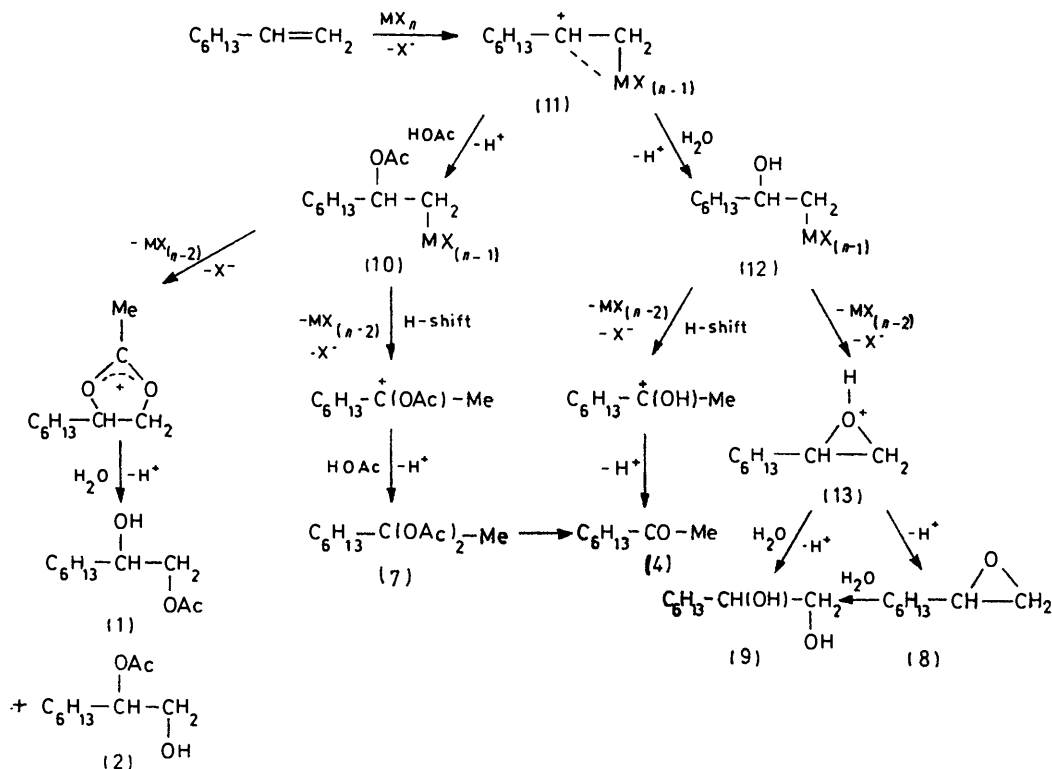
⁸ M. S. Kharasch, H. N. Friedlander, and W. H. Urry, *J. Org. Chem.*, 1951, **16**, 533.

⁹ W. A. Mosher and C. L. Kehr, *J. Amer. Chem. Soc.*, 1953, **75**, 3172; D. Benson, L. H. Sutcliffe, and J. Walkley, *ibid.*, 1959, **81**, 4488; R. O. C. Norman and M. Poustie, *J. Chem. Soc. (B)*, 1968, 781.

¹⁰ R. Criegee, in 'Oxidation in Organic Chemistry,' part A, ed. K. B. Wiberg, Academic Press, New York, 1965, p. 277.

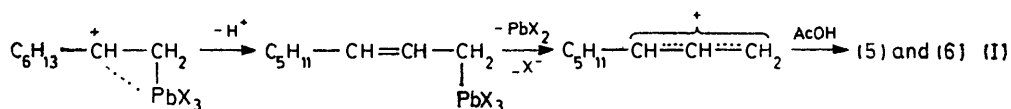
and production of an acetoxonium ion; adventitious⁴ or added water then gives the hydroxy-acetate. The diacetate is likely to be formed by slow esterification of (1) and (2),⁴ but its production directly from (10) cannot be ruled out. Of the other products from the lead(IV) oxidation, (7) could arise by hydride shift concomitant with cleavage of the carbon-lead bond and might, in part, decompose to give octan-2-one.⁴ An alternative

lack of these products from the analogous thallium system unless a much greater degree of interaction between the metal atom and the carbonium ion centre inhibits the loss of a proton from (11; M = Tl, $n = 3$). A more satisfactory explanation is that (5) and (6) are the result of a radical process. Lead(IV) carboxylates are known to generate radicals on decomposition^{8,11,12} and such intermediates could abstract hydrogen atoms



SCHEME 1

M = Pb or Tl; X = AcO or HO; $n = 4$ or 3



route to the latter compound, at least in experiments 2—4, is the competition of water with acetic acid for the carbonium ion (11; M = Pb, $n = 4$) to give the hydroxy-lead adduct (12; M = Pb, $n = 4$); this would be expected to undergo hydride shift more readily than the analogous acetoxonium adduct (10; M = Pb, $n = 4$). These routes are summarised in Scheme 1.

For the allylic acetates (5) and (6) an ionic mode of formation is possible, *e.g.* via an allyl-lead species derived from (11; M = Pb, $n = 4$) [reaction (1)], but if this path is followed it is difficult to account for the

from the allylic position in oct-1-ene. Oxidation of the resultant radical by lead(IV) * would lead, after reaction with the solvent, to (5) and (6). As there is no evidence that thallium(III) acetate decomposes homolytically we would not expect allylic acetates to be formed in this way from that reagent. We will return later to the problem of the formation of allylic compounds from olefins.

Comparing experiment 3 with experiment 5 shows that the two oxidants give very similar results. [Experiment 3 is chosen for comparison since, as thallium(III) sesquihydrate was employed, an extra 7.5 mmol of water is available from this source.] On increasing the

* Lead(IV) readily oxidises radicals which give stabilised carbonium ions.^{12,13}

¹¹ J. K. Kochi, *J. Amer. Chem. Soc.*, 1965, **87**, 1811, 3609.

¹² J. K. Kochi, J. D. Bacha, and T. W. Bethea, *J. Amer. Chem. Soc.*, 1967, **89**, 6538.

¹³ M. Lj. Mihailovic and R. E. Partch, in 'Selective Organic Transformations,' vol. 1, ed. B. S. Thyagarajan, Wiley, New York, 1972, p. 97.

ratio of water to acetic acid the yield of (4) rises at the expense of (1) + (2) and (3), in line with the greater likelihood of the ion (11; $M = Tl, n = 3$) giving (12; $M = Tl, n = 3$) rather than (10; $M = Tl, n = 3$). At high concentrations of water, diol formation rapidly becomes important. A check experiment showed that, under the reaction conditions, the epoxide undergoes extensive ring opening to give predominantly diol together with some hydroxy-acetate. We assume therefore, by analogy with the participation of a neighbouring methoxy-substituent in the solvolysis of methoxy-thallium adducts,¹ that the oxonium ion (13) is formed and leads *via* (8) to the diol. Even so, the lack of a direct relationship between the yield of (4) and of (8) + (9) suggests either that increased solvent polarity favours the formation from (12) of (13) or that there is an alternative route to the diol, possibly the direct replacement of the metal substituent by water.

Ouellette has pointed out that the earlier studies of the oxidation of non-cyclic olefins by thallium(III) in aqueous acetic acid contain a number of apparent contradictions.¹⁴ Our results enable us to clarify many of these inconsistencies. Grinstead¹⁵ noted that hex-2-ene gave hexane-2,3-diol acetate and hexan-2-one. No diol formation was reported* but, surprisingly, ethylene failed to react. Henry's work,¹⁶ on the other hand, was primarily kinetic and use was made of a large excess of water and an acid catalyst. Each olefin

comparable yields of 1,2-epoxypropane and acetone. Hydroxy-acetates are not mentioned though they are formed in solvents with less acetic acid. The method of removal of epoxide would give little chance for its conversion into diol.

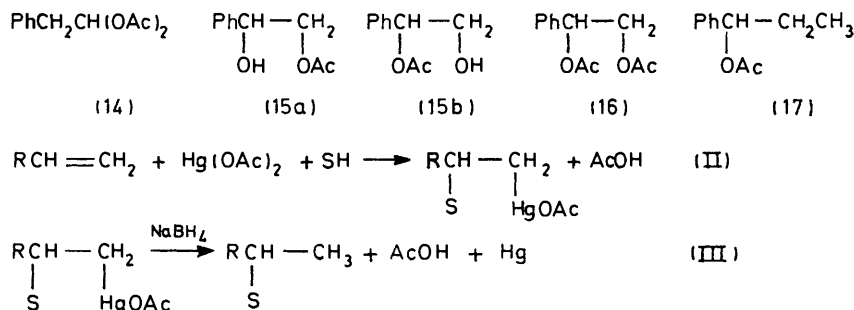
To check whether the addition of small amounts of water to acetic acid is a general method of increasing the yield of ionic products in lead(IV) oxidations, we repeated the experiments with styrene. At 60° styrene has been shown to give roughly equal amounts of ionic [(14) plus (15) and some (16)] and of radical [(17) plus the remainder of (16)] products.³ As expected, the addition of 2 equiv. of water to the system increases the yield of (15) primarily at the expense of (17) (Table 3) but the effect is not as marked as for oct-1-ene.

TABLE 3

Products from the oxidation of styrene (5 mmol) by lead(IV) acetate (5 mmol) in acetic acid (10 ml) at 60°

Added H ₂ O (mmol)	Time (h)	Products (%)			
		(14)	(15)	(16)	(17)
	3	32	5	12	30
10	3	28	17	10	18

Olefins react with mercury(II) acetate in a number of nucleophilic solvents, SH, to give metal adducts [reaction (II)] which, on reduction by sodium borohydride, give, efficiently, products in which formally SH has been added across the double bond [reaction (III)].¹⁹



gave two products, a glycol and a carbonyl compound. The diols were supposed to arise directly. Certainly they do not derive from hydroxy- or di-acetates but, since cleavage of the corresponding epoxides in perchloric acid is extremely fast,¹⁷ it is possible that oxiran intermediates were overlooked. Kruse *et al.*¹⁸ found, under conditions similar to experiment 10, that propene gave

* Experimental details are lacking but it would appear that g.l.c. was not employed in estimating the product yields. This, or the significant solubility of the diol in water, may account for the failure to observe it.

† However, the use of high temperatures in the reaction of olefins with mercury(II) acetate can give synthetically useful yields of allylic acetates;²¹ presumably acetoxy-mercury adducts are formed initially (*cf.* ref. 22).

¹⁴ R. J. Ouellette, in 'Oxidation in Organic Chemistry,' part B, ed. W. S. Trahanovsky, Academic Press, New York, 1973, p. 135.

¹⁵ R. R. Grinstead, *J. Org. Chem.*, 1961, **26**, 238.

¹⁶ P. M. Henry, *J. Amer. Chem. Soc.*, 1965, **87**, 4423; 1966, **88**, 1597.

¹⁷ J. B. Ley and C. A. Vernon, *J. Chem. Soc.*, 1957, 3256.

¹⁸ W. Kruse and T. M. Bednarski, *J. Org. Chem.*, 1971, **36**, 1154.

However, there are no reports of the synthetic use of this procedure for the addition of carboxylic acids despite the frequent references²⁰ to the formation of acyloxy-mercury adducts.† The explanation for this is

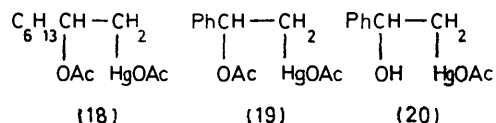
¹⁹ H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, 1969, **91**, 5646; H. C. Brown and J. T. Kurek, *ibid.*, p. 5647; H. C. Brown and P. J. Geoghegan, *J. Org. Chem.*, 1970, **35**, 1844; J. J. Périé and A. Lattes, *Bull. Soc. chim. France*, 1970, 583; D. H. Ballard and A. J. Bloodworth, *J. Chem. Soc. (C)*, 1971, 945; J. J. Périé, J. P. Laval, J. Roussel, and A. Lattes, *Tetrahedron*, 1972, **28**, 675; A. J. Bloodworth and G. S. Bylina, *J.C.S. Perkin I*, 1972, 2433; A. J. Bloodworth and R. J. Bunce, *ibid.*, p. 2787.

²⁰ A. G. Brook and G. F. Wright, *Canad. J. Res.*, 1950, **28B**, 623 (*Chem. Abs.*, 1951, **45**, 7031e); K. C. Pande and S. Winstein, *Tetrahedron Letters*, 1964, 3393; K. Ichikawa, O. Itoh, T. Kawamura, M. Fujiwara, and T. Ueno, *J. Org. Chem.*, 1966, **31**, 447; A. Factor and T. G. Traylor, *ibid.*, 1968, **33**, 2607.

²¹ W. Treibs and H. Bast, *Annalen*, 1949, **561**, 165; W. Treibs, G. Lucius, H. Kögler, and H. Breslau, *ibid.*, 1953, **581**, 59; Z. Rappoport, P. D. Sleezer, S. Winstein, and W. G. Young, *Tetrahedron Letters*, 1965, 3719; Z. Rappoport, L. K. Dyal, S. Winstein, and W. G. Young, *ibid.*, 1970, 3483; Z. Rappoport, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, 1972, **94**, 2320.

²² S. Wolfe, P. G. C. Campbell, and G. E. Palmer, *Tetrahedron Letters*, 1966, 4203.

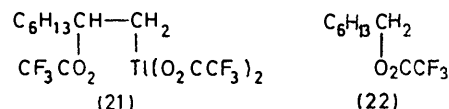
suggested by our recent observation⁶ that the organomercurial (18), obtained in high yield from oct-1-ene, reacts with borohydride to give not only 1-methylheptyl acetate (40%) but also octan-2-ol (31%) and oct-1-ene (ca. 26%). We believe that the octanol results from reduction of the ester function *before* loss of the mercury substituent, an organomercury hydride²³ probably being the key intermediate. We have found that styrene behaves similarly. Its reaction with mercury(II) acetate appeared to give exclusively (19) [the n.m.r.



spectrum, in which the aliphatic protons are clearly distinguishable from those of (20), showed no trace of the latter]; reduction gave 1-phenylethyl acetate (48%) and 1-phenylethanol (23%) together with a considerable amount of styrene. However, the yield of the acetate could be improved to 64%, at the expense of the alcohol (10%), by the use of dichloromethane as solvent for the reduction step.

Oxidation of Oct-1-ene in Trifluoroacetic Acid.—We have shown that thallium(III) trifluoroacetate reacts rapidly with oct-1-ene at room temperature in anhydrous

and (2) (Scheme 2). Since the epoxide (8) is rapidly converted, in trifluoroacetic acid, into the hydroxy-esters (24) and (25) which were not detected, it must be formed during work-up; we infer that the thallium adduct (26) is stable until work-up.⁶ The absence of (24) and (25) and the low yield of the ketone (4) suggest that there is little if any incorporation of hydroxy at C-2 of the olefin, despite the potential availability of at least as much water as acetic acid in the system (since the thallium salt was the sesquihydrate); possibly the water remains co-ordinated to thallium. However, there was evidence for such incorporation when a large excess of water was present (experiment 13). Not only were the hydroxy-esters (24) and (25) formed in small yield but there was a large increase in the yield of ketone, mainly at the expense of the hydroxy-acetates (1) and (2). Evidently the initial carbonium ion (27) is now mainly trapped by water with formation of the adduct (28) and thence (4) by hydride shift.



The reaction of oct-1-ene with lead(IV) acetate in trifluoroacetic acid (experiment 14) is notably different

TABLE 4

Products from the oxidation of oct-1-ene (10 mmol) by thallium(III) or lead(IV) (10 mmol) in trifluoroacetic acid (10 ml) at 25°

Expt.	Oxidant	Time (min)	Products (%)							
			C ₈ H ₁₃ CH=CH ₂ (8)	(4)	(32)	(9)	(24) + (25)	(1) + (2)	(22)	
11	Tl(O ₂ CCF ₃) ₃	<i>a</i>	<1	16	34		40	2		
12	Tl(OAc) ₃	10	4.4	13	12		21		47	1
13 ^b	Tl(OAc) ₃	15	Trace	0.8	46		31	3	8	Trace
14	Pb(OAc) ₄	10	7		4.6	21			5	5.6

^a Near instantaneous; ref. 6. ^b Solvent: 1:1 (v/v) trifluoroacetic acid-water.

solvents to give a stable adduct (21) which undergoes fast decomposition during aqueous work-up to give (4), (8), and (9).⁶ A typical product distribution, after work-up, is shown in experiment 11 (Table 4). However, the reaction with thallium(III) acetate in trifluoroacetic acid is not only slower, consistent with the reduced electrophilicity of the oxidant²⁴ and a slow rate of ligand exchange¹ [permitting the addition of a proton, and thence formation of 1-methylheptyl trifluoroacetate (22), to compete with oxidation to a limited extent], but also gives a strikingly different product distribution (experiment 12). From the predominance of the hydroxy-acetates (1) and (2), we infer that the cation formed from the olefin and thallium(III) reacts preferentially with the stronger nucleophile, acetic acid, rather than the much more abundant trifluoroacetic acid, giving mainly (23) and thence (1)

from that with thallium(III) acetate in giving octanal (32) as major product.* 1,2-Epoxyoctane and octane-1,2-diol did not give octanal under the reaction conditions, and there seemed only two other possible routes to this compound: hydride-shift during heterolysis of the 'anti-Markovnikov' adduct (29), and alkyl migration during decomposition of the expected Markovnikov adduct (31). Anti-Markovnikov addition might occur if the hexyl group were to hinder nucleophilic attack on an intermediate plumbonium ion such as (30) (*cf.* the reaction of 3,3-dimethylbut-1-ene with bromine²⁵). If so, then the corresponding intermediate from 1,1-diheptylethylene would be at least as likely to yield the 'anti-Markovnikov' adduct and thence diheptylacet-aldehyde. However, we could not detect this aldehyde as a product from 1,1-diheptylethylene under the same conditions as experiment 14; the major product was

* The yields in this experiment were not easily reproducible. The rate of admixture of the reagents appeared to be a critical factor. The values recorded are typical.

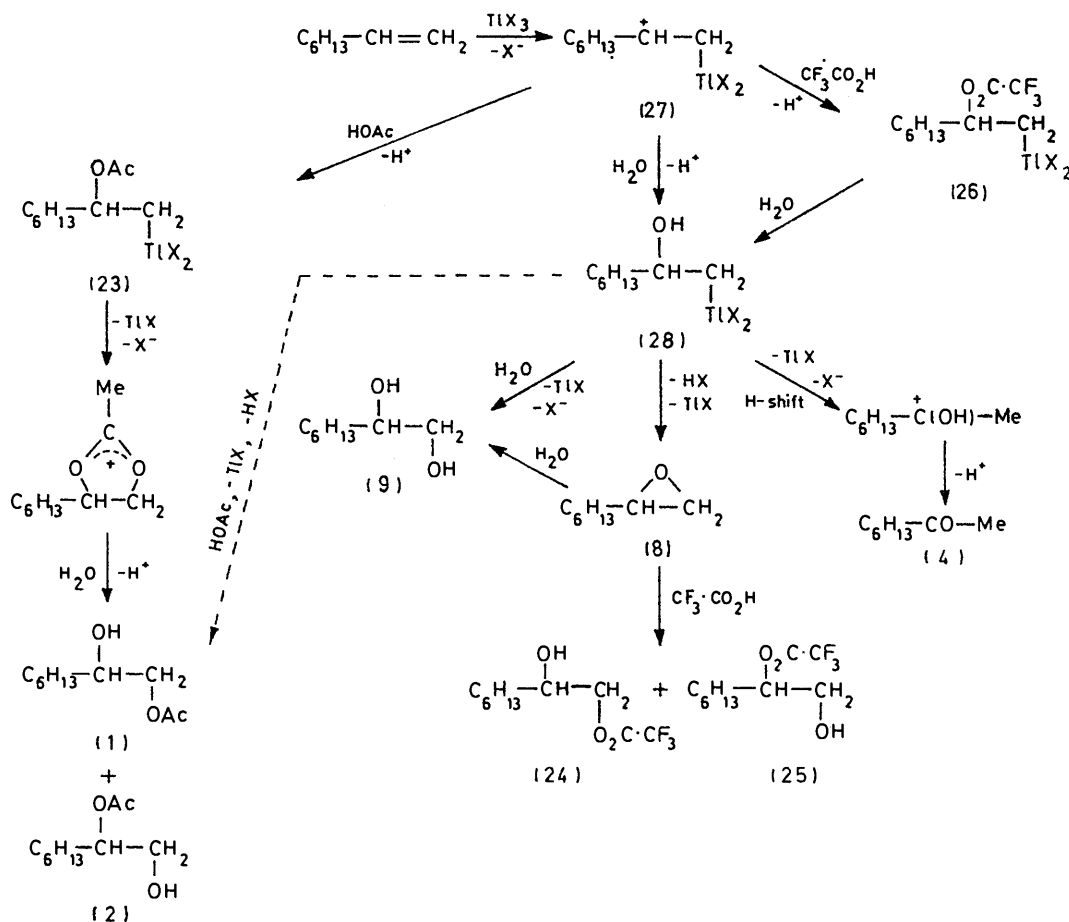
²³ D. J. Pasto and J. A. Gontarz, *J. Amer. Chem. Soc.*, 1969, **91**, 719.

²⁴ 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.

²⁵ W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, 1957, **79**, 3469.

hexadecan-8-one (29%), together with unchanged olefin and other products analogous to those from oct-1-ene, so that we conclude that an alkyl-shift occurs both in this case and for oct-1-ene [reaction (IV)].*

appropriate to alkyl-migration in preference to (34), and that the lability of the C-Pb bond is such that the rate of heterolysis is greater than that of conformational interchange; with the more stable organo-thallium



The problem then posed is why should an organo-lead adduct such as (31) undergo an alkyl-shift whereas analogous organo-thallium adducts do not, either in our or in other rearrangement-prone systems.³² We can only suggest that (31) exists in the conformation (33)

* Whilst aryl rearrangements on lead(IV) oxidations of suitable olefins are well documented^{3,4,26-28} particularly in trifluoroacetic acid,²⁹ alkyl migrations appear to be confined to the ring contraction and expansion of alicyclic compounds^{26,27,30,31} in which the migrating group should be preferably oriented *anti* to the departing lead substituent.

† The oxidation of cyclohexene, which could also give stereochemical information, has been studied previously. However, in this case the bulk of the metal substituent is likely to result in this group preferentially occupying an equatorial position in the alicyclic adduct, subsequent decomposition then resulting in ring contraction (*anti*-shift) and loss of stereochemical information. This certainly seems to be the case for lead(IV) oxidations.^{27,30} What little quantitative information is available on 1,2-adducts suggests that *cis*- and *trans*-diacetates are formed in approximately equal amounts,³⁰ but the yields of these products are low. Some stereochemical results have also been reported from the oxidation of 1-phenylpropene⁴ but here a complicating factor is the stabilisation of the initial carbonium ion centre by the phenyl substituent.

adducts, this is not the case, so that the better migrating group, hydride, shifts even though this is only possible through the less-favoured conformation.

Oxidation of trans-Oct-4-ene.—The products of oxidation of oct-1-ene give no information on the stereochemistry involved in the formation and the decomposition of the organometallic adduct. We chose to use oct-4-ene in order to study this aspect.† Oxidation

²⁶ R. Criegee, P. Dimroth, K. Noll, R. Simon, and C. Weis, *Chem. Ber.*, 1957, **90**, 1070.

²⁷ H.-J. Kabbe, *Annalen*, 1962, **656**, 204.

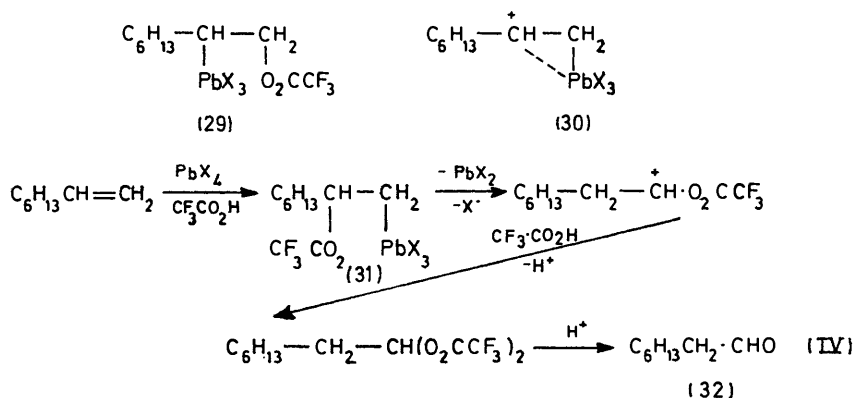
²⁸ Y. Yukawa and N. Hayashi, *Bull. Chem. Soc. Japan*, 1966, **39**, 2255; R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1967, 604.

²⁹ A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1973, 35.

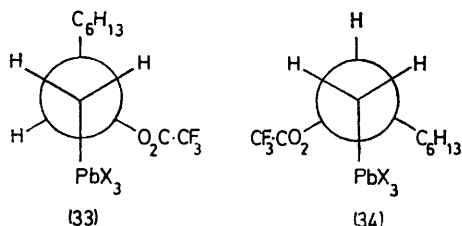
³⁰ C. B. Anderson and S. Winstein, *J. Org. Chem.*, 1963, **28**, 605.

³¹ W. Hüchel and H. G. Kirschner, *Chem. Ber.*, 1947, **80**, 41; P. Naffa and G. Ourisson, *Bull. Soc. chim. France*, 1954, 1115; Y. Matsubara, *Nippon Kagaku Zasshi*, 1955, **76**, 1088; Y. Heya, *ibid.*, 1960, **81**, 166; S. Wakabayashi, *Kogyo Kagaku Zasshi*, 1960, **63**, 627 (*Chem. Abs.*, 1962, **56**, 7165c).

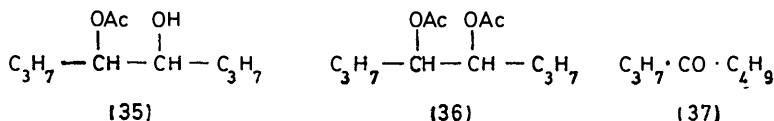
³² A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1973, **95**, 3635.



by lead(IV) acetate in acetic acid gave a disappointingly low accountability, a feature which seems to characterise



many lead(IV) oxidations in this solvent system. The major products were the hydroxy-acetates (35) and an



allylic acetate (39), isolated by preparative g.l.c. and discussed in more detail later. Minor products were the diacetates (36) and octan-4-one (37). Compounds (35) were determined by acetylation of the crude reaction product and measurement of the resultant increases in the yields of diacetates. These results are in Table 5 (experiment 15).

TABLE 5

Products from the oxidation of *trans*-oct-4-ene (10 mmol) in acetic acid (20 ml) at 60°

Expt.	Oxidant (10 mmol)	Time (h)	Products (%)			Ratio <i>erythro</i> : <i>threo</i> (36)		
			(39)	(36)	(37)			
15	Pb(OAc) ₄	a	45	12	1.8	Trace	4.0	
		b		c	16	c		7.9
		c			0.95	c		4.0
16	Pb(OAc) ₄	a	45	7.6	0.35	Trace	1.9	
		b		c	8.9	<0.5		0.25
		c			33	c		0.25
17	Tl(OAc) ₃	a	240	41	8.9	<0.5	0.25	
		b		c	33	c		0.25
		c						

^a After work-up. ^b After acetylation of crude product. ^c Not measured. ^d Under nitrogen.

There appears to be considerable stereoselectivity in formation of hydroxy-acetates as judged by the ratio of *erythro*- to *threo*-diacetate produced on acetylation. However, the major isomer is not the *threo*-compound expected of overall *syn*-addition *via* plumbonium and acetoxonium ion intermediates (Scheme 3); instead,

the *erythro*-isomer predominates. The overall yield of hydroxyacetate is no greater than that which might be expected of autoxidation⁴ and, indeed, if hydroxyacetates result from (acid-catalysed) nucleophilic attack on the epoxide, the *erythro*-isomer is to be expected (Scheme 4). To check this possibility reaction was repeated under nitrogen. The results (experiment 16) appear to confirm that autoxidation is the major source of (35). That the diacetates present before acetylation do not come exclusively from (35) is suggested by the change in stereoisomeric ratio on acetylation. Under the conditions of the experiment they are most unlikely to originate directly *via* an ionic reaction [sufficient water is

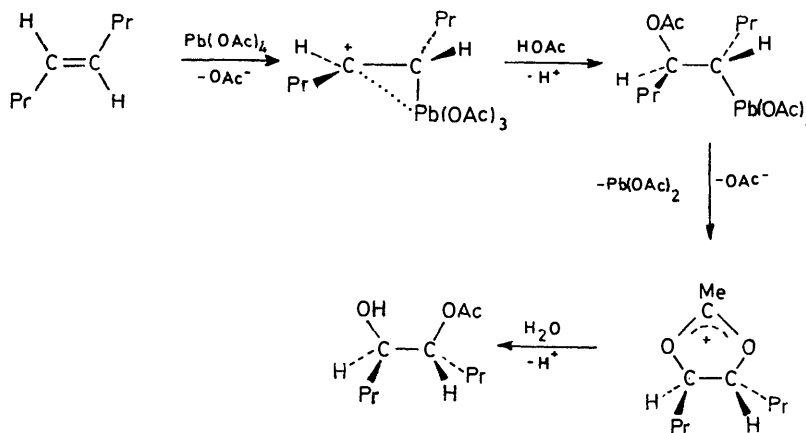
present to divert all acetoxonium ions to (35)⁴] and a probable route is the radical addition sequence identified for aryl olefins.^{3,4}

Leaving for the present the problem of allylic acetoxylation, we next consider the stereochemical consequences of the oxidation of *trans*-oct-4-ene by thallium(III) acetate. The major products were once again (35) and (39). The ratio of the stereoisomeric diacetates does not change on acetylation of the crude reaction product, strongly suggesting that the diacetate present before work-up originates exclusively by esterification of (35). Interestingly there is no evidence from this ratio that autoxidation is an important side reaction in experiment 17 despite the greatly increased reaction time. This could be because thallium(III) is a less efficient autoxidation catalyst than lead(IV) but it is much more probable that the bulk of the olefin is rapidly converted into the organothallium adduct which decomposes only slowly,¹ so that there is little olefin available for autoxidation. Stereochemical control is not absolute in the formation of hydroxy-acetates, but the predominance of the *threo*-isomer is consistent with a mechanism analogous to Scheme 3, the presence of the *erythro*-compound perhaps reflecting an interaction between the C-5 atom and the metal substituent sufficiently weak as not completely to prevent rotation about the C-4-C-5 bond.

These results are in broad agreement with those from cyclohexene oxidation. With thallium(III) a considerable degree of stereochemical control is observed,^{30,33} but with lead(IV) a low yield of hydroxy-acetates and diacetates is characterised by lack of stereoselectivity.^{30,34}

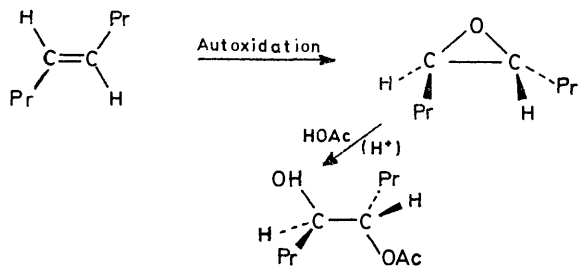
Allylic acetoxylation is a more difficult problem to unravel. Both ionic and radical mechanisms can be postulated for the formation of allylic compounds but,

that *cis*- and *trans*-isomers of the same olefin would show nearly identical mass spectra, we believe that our product is a mixture of (39a) and (39b). This is consistent with the allylic acetate arising *via* an allylic carbonium ion. Further, the allylic acetate produced by acetolysis of the bromide from *N*-bromosuccinimide with oct-4-ene and that from lead(IV) oxidation of the same olefin exhibited mass spectral-g.l.c. behaviour



SCHEME 3

since there are no reports of thallium(III) systems reacting by radical routes despite the extensive study in recent years of this oxidant,³⁵ a heterolytic process for allylic acetoxylation would seem more probable in this case. It is noteworthy that in only two other



SCHEME 4

instances of olefin oxidation by thallium(III) have allylic products been detected^{27,30,33} and then only in small amounts. The two ionic routes envisaged for acetoxylation are in Scheme 5. Route (a) would be expected to result in the formation of two allylic acetates (ignoring geometric isomers) whilst route (b) would produce only one.

The g.l.c. trace showed only one component assignable as an allylic acetate. However, g.l.c. comparison with an authentic sample of *trans*-1-ethylhex-2-enyl acetate showed that our peak was somewhat broader than expected and repeated mass spectral scanning confirmed it to be not homogeneous. All the major ions of the authentic compound were present but their relative intensities varied across the scan, although no new ions appeared. On the reasonable assumption

identical with that of the sample from thallium(III) oxidation, consistent with a common intermediate in all three reactions.

We conclude, therefore, that it is most probable that allylic oxidation by thallium(III) occurs *via* route (a) of Scheme 5 but we are unable to offer a fully acceptable explanation of why a carbonium ion such as (38) should lose a proton so easily whereas analogous ions from terminal olefins react exclusively by uptake of an acetate group. 'Steric hindrance' seems too facile a reason, though it should be noted that a *cis*-olefin such as cyclohexene, where such constraints ought to be reduced, is intermediate between oct-1-ene and *trans*-oct-4-ene in its yield of allylic products.^{30,33}

Superficially, lead(IV) resembles thallium(III). Thus, allylic products are formed in insignificant yield from terminal olefins yet for oct-4-ene such substitution is of major importance. However, it would be unsafe to assume that (39) results from a heterolytic reaction for there is no evidence for the mediation of an ion analogous to (38). If such a species were formed, we should expect it to undergo nucleophilic attack to give 1,2-adducts, yet not more than 1% of (35) can arise from a path other than autoxidation (experiment 16). On the other hand, as mentioned earlier, lead(IV) can produce allylic compounds homolytically; the initial allylic radical being oxidised to the carbonium ion and thus leading to the same ratio of (39a) to (39b) as was obtained in the thallium(III) and solvolytic systems. Such a view is consistent with the observation that allylic

³³ J. B. Lee and M. J. Price, *Tetrahedron*, 1964, **20**, 1017.

³⁴ A. A. Mahmood, D. Phil. Thesis, York, 1970.

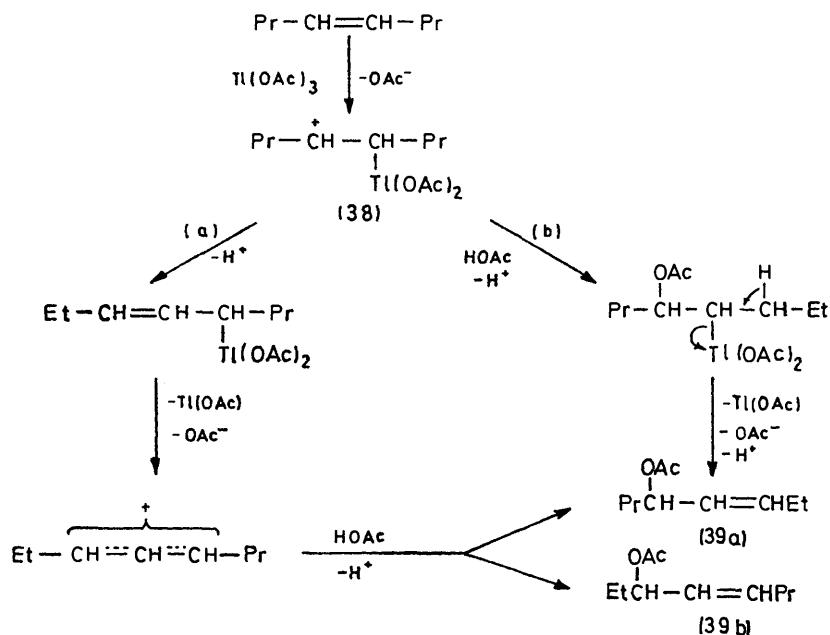
³⁵ A. McKillop and E. C. Taylor, *Chem. in Britain*, 1973, **9**, 4.

oxidation of cyclohexene by lead(IV) acetate involves a symmetrical intermediate.³⁶

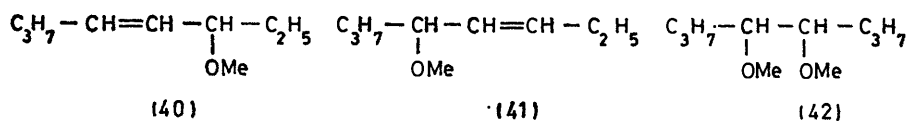
Like acetic acid, methanol proved an unsatisfactory solvent for probing the stereochemistry of the reaction of *trans*-oct-4-ene with lead(IV) acetate. The lead(IV) was consumed in 2 h at 60° but accountability was even lower than in acetic acid. Not all the large number of products could be adequately resolved by g.l.c. but the major one (*ca.* 6%) was an allylic methoxy-compound assumed, on the basis of major fragments at *m/e* 113 and 99 in the mass spectrum, to be a mixture of (40) and (41). Also present were octan-4-one (3%) and a

(*ca.* 3.5%) were obtained together with most of the minor products from lead(IV) oxidation. We can only assume that the low accountability with both reagents is the result of concomitant oxidation of the solvent to formaldehyde³⁷ and reflects the difficulty of attack by the bulky metal electrophiles on internal acyclic olefins.

Finally, our earlier conclusions for monosubstituted olefins based on a methanol solvent system can be extended to other solvents; that is, an initial organometallic adduct undergoes heterolysis with or without participation of a substituent on the adjacent carbon atom. In acetic acid this participation leads to an



SCHEME 5



dimethoxy-adduct which g.l.c.-m.s. scanning suggested to be a mixture (total yield *ca.* 5%) of the 4,5-dimethoxy-adduct (42) and a dimethyl acetal (presumably that from octan-4-one). However, we cannot tell whether (42) is itself a mixture of diastereoisomers or is a single compound and therefore cannot solve the problem of the stereochemistry of addition. No other products were present in greater than 2% yield but residual olefin accounted for a further 17% of the starting material.

Thallium(III) acetate under the same conditions yielded a very similar product distribution and, surprisingly for a thallium(III) oxidation, the accountability was scarcely better than with lead(IV); methoxyoctenes (*ca.* 8% yield), octan-4-one (4%), and dimethoxyoctanes

acetoxonium ion and thence to high yields of hydroxy-acetates. However, steric factors appear to be critical for these bulky electrophiles and alternative modes of reaction assume major importance with internal olefins. This is particularly true for lead(IV) oxidations where there appears to be little if any evidence for normal adduct formation.

EXPERIMENTAL

The analytical techniques and a number of the compounds employed in this study have been described previously.^{1,3,6} Octanal and *trans*-oct-4-ene (Emanuel) and 1-phenylethanol (Fisons) were commercial samples. 1-Phenylethyl acetate was prepared as for 1-phenylpropyl acetate.³ *trans*-1-Ethylhex-2-enyl acetate was the generous gift of Professor K. B. Sharpless.

Other Materials.—1-Pentylallyl acetate. Oct-1-en-3-ol was

³⁶ K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, 1964, **29**, 3353.

³⁷ B. Davies and A. Lethbridge, forthcoming publication.

prepared by a modification of the method of Rosenmund and Bach.³⁸ Acrolein (18.6 g) in dry ether (200 ml) was added to a solution of pentylmagnesium bromide from 1-bromopentane (50 g) and magnesium turnings (8.5 g) in dry ether (200 ml). After addition the mixture was refluxed for 0.5 h, cooled, and poured into ammonium chloride solution; the ether layer was dried (MgSO₄), the solvent removed, and the residue distilled to give oct-1-en-3-ol (3.1 g, 7%) as a liquid, b.p. 70° at 13 mmHg (lit.,³⁹ 78—79° at 20 mmHg); τ 4.10 (1H, ddd, J 6, J' 9, J'' 16.5 Hz, $-\text{CH}=\text{}$), 4.65—5.10 (2H, m, $=\text{CH}_2$), 5.96br (1H, m, CHOH), 7.60 (1H, s removed by D₂O, OH), and 8.10—9.35 (11H, aliphatic envelope).

The alcohol (3 g) was acetylated as described below for octane-4,5-diyl diacetates to give 1-pentylallyl acetate (3.1 g, 78%) as a liquid, b.p. 78° at 11 mmHg (lit.,⁴⁰ 76—77° at 10 mmHg); τ 4.26 (1H, ddd, J 5.5, J' 9, J'' 18 Hz, $-\text{CH}=\text{}$), 4.60—5.00 (3H, m, $=\text{CH}_2$ and $-\text{CHOAc}$), 7.95 (3H, s, OAc), and 8.10—9.25 (11H, aliphatic envelope).

2-Heptylnon-1-ene. Pentadecan-8-ol was prepared by adding, with stirring, a solution of octanal (11.5 g) in dry ether (50 ml) to a cooled solution of heptylmagnesium bromide from heptyl bromide (17.9 g) and magnesium (2.7 g) in dry ether (50 ml) during 0.5 h. After refluxing for a further 0.5 h, saturated ammonium chloride solution was added and the ether layer was dried (MgSO₄). Removal of the solvent left crude pentadecan-8-ol (18 g). Without further purification this was oxidised by a modification of the method of Macbeth and Mills.⁴¹ A mixture of the crude alcohol and aqueous sodium dichromate (6 g in 25 ml water) was stirred at 60° whilst 98% sulphuric acid (16 g) was added slowly. After 2 h the solution was cooled, water added, and the mixture extracted with ether. The extracts were dried (MgSO₄) and the solvent removed to give pentadecan-8-one (17 g, 69%) as plates, m.p. 40—41° (from ethanol) (lit.,⁴² 40°), τ 7.63 (4H, t, J 6.8 Hz, CH₂CO) and 8.20—9.40 (26H, aliphatic envelope).

A solution of phenyl-lithium (0.1 mol) in dry ether (100 ml) was added dropwise to a stirred suspension of methyltriphenylphosphonium bromide (36 g) in dry ether (200 ml) under nitrogen. A yellow colour developed which became clear orange after addition was complete. To this solution was added, during 1 h, pentadecan-8-one (22.5 g) in dry ether (200 ml). A thick white precipitate formed, the solution was refluxed overnight, and water was added. The organic layer was dried (MgSO₄) and the solvent evaporated off to give a grey oil. This was passed down an alumina column with light petroleum (b.p. 40—60°) as eluant and the material obtained after evaporation of the solvent distilled to give 2-heptylnon-1-ene (15 g, 67%) as a liquid, b.p. 94° at 0.4 mmHg; τ 5.34 (2H, s, $=\text{CH}_2$) and 7.80—9.40 (30H, aliphatic envelope) (Found: C, 86.0; H, 14.3. C₁₆H₃₂ requires C, 85.7; H, 14.3%).

Hexadecan-8-one was obtained in a similar manner to pentadecan-8-one from octanal (12.8 g), octyl bromide (19 g), and magnesium (2.7 g). Recrystallisation from light petroleum (b.p. 40—60°) gave hexadecan-8-one (16.7 g, 70%) as plates, m.p. 36—37° (lit.,⁴³ 37°); τ 7.63

(4H, t, J 7.2 Hz, CH₂CO) and 8.30—9.40 (28H, aliphatic envelope).

threo-2-Hydroxy-1-propylpentyl acetate. This was prepared by a 'wet' Prevost reaction on *trans*-oct-4-ene following the method of Woodward and Brucher,⁴⁴ and was obtained as a liquid (66%), b.p. 116—118° at 12 mmHg; τ 5.16 [1H, ddd, J 4.5, J' 6.0, J'' 6.5 Hz, $-\text{CH}(\text{OAc})-$], 6.41br (1H, s, $-\text{CHOH}-$), 7.69br (1H, d removed by D₂O, OH), 7.93 (3H, s, OAc), and 8.20—9.30 (14H, aliphatic envelope) (Found: C, 63.5; H, 10.6. C₁₆H₃₀O₃ requires C, 63.8; H, 10.6%).

DL-1,2-Dipropylethylene diacetate. The foregoing *threo*-hydroxy-acetate (1 g) was heated under reflux for 1 h with anhydrous sodium acetate (1 g) and acetic anhydride (10 ml). The cooled solution was poured into water and the ether extract was washed with sodium carbonate solution and dried (MgSO₄). Evaporation of the solvent gave the DL-diacetate (1.0 g, 82%) as a liquid, b.p. 120° at 11 mmHg (lit.,⁴⁵ 110° at 5.5 mmHg); τ 4.98br (2H, m, CH), 7.93 (6H, s, OAc), and 8.25—9.25 (14H, aliphatic envelope).

meso-1,2-Dipropylethylene diacetate. *trans*-Oct-4-ene (5.6 g) was converted into *meso*-octane-4,5-diol by the method of Vogel⁴⁶ with formic acid (30 ml) and 30% hydrogen peroxide (7 ml). The diol was obtained as leaflets (4.9 g, 67%), m.p. 121—122° (lit.,⁴⁵ 123.5—124.5°). Refluxing the diol (2.5 g) for 2 h with anhydrous sodium acetate (5 g) and acetic anhydride (40 ml) followed by work-up as above gave the *meso*-diacetate (3.4 g, 87%) as a liquid, b.p. 114° at 11 mmHg (lit.,⁴⁵ 100° at 5 mmHg); n.m.r. spectrum identical with that of the DL-isomer.

Octan-4-one. *trans*-Oct-4-ene (12 g) was stirred with mercury(II) acetate (31 g) in tetrahydrofuran (40 ml) and water (20 ml) at 60° for 3 h. 2M-Sodium hydroxide solution (40 ml) was then added followed by an alkaline solution of sodium borohydride (1.5 g in 30 ml water). The organic layer was dried (MgSO₄). Evaporation of the solvent and distillation of the residue gave octan-4-ol (11 g, 79%) as a liquid, b.p. 65° at 8 mmHg (lit.,⁴² 71° at 10 mmHg). This alcohol (5 g) was heated with a mixture of sodium dichromate (2 g) and 98% sulphuric acid (5 ml) at 50° for 2 h. The ether extract was dried (MgSO₄), the solvent removed, and the residue distilled to give octan-4-one (3.5 g, 71%) as a liquid, b.p. 48° at 9 mmHg (lit.,⁴² 70° at 26 mmHg); τ 7.58 (4H, t, J 6.8 Hz, CH₂CO), 8.05—9.00 (6H, ms, CH₂), and 9.08 (6H, t, J' 7.0 Hz, CH₃).

Oxidations.—These were carried out in the appropriate solvent system using the procedures described previously.^{1,3,4,6,29} Some of the products for which no authentic samples were available were identified from their g.l.c.—mass spectra. These were 1-propylpent-2-enyl acetate plus 1-ethylhex-2-enyl acetate (isolated by preparative g.l.c.); τ 3.65—5.0 (3H, m, $-\text{CH}-\text{CH}=\text{}$), 8.02 (s, OAc), and 7.4—9.3 (aliphatic envelope) (total 15H); m/e 170 (M⁺, 6%), 141 (6, $M - \text{C}_2\text{H}_5$), 128 (36, $M - \text{CH}_2\text{CO}$), 127 (14, $M - \text{C}_3\text{H}_7$ and $M - \text{CH}_3\text{CO}$), 99 (39, $M - \text{CH}_2\text{CO} - \text{C}_2\text{H}_5$), 85 (40, $M - \text{CH}_2\text{CO} - \text{C}_3\text{H}_7$), 81 (29, 99 - H₂O), 67 (24, 85 - H₂O), 55 (21, C₄H₇⁺), and 43 (100, CH₃CO⁺)

⁴³ R. E. Bowman and W. D. Fordham, *J. Chem. Soc.*, 1951, 2753.

⁴⁴ R. B. Woodward and F. W. Brucher, *J. Amer. Chem. Soc.*, 1958, 80, 209.

⁴⁵ W. G. Young, Z. Jasaitis, and L. Levanas, *J. Amer. Chem. Soc.*, 1937, 59, 403.

⁴⁶ A. I. Vogel, 'Practical Organic Chemistry,' 3rd edn., Longmans, London, 1966, p. 894.

³⁸ K.-W. Rosenmund and H. Bach, *Chem. Ber.*, 1961, 94, 2394.

³⁹ T. Ueda, *Nippon Kagaku Zasshi*, 1962, 83, 338.

⁴⁰ G. Smets, *Trav. lab. chim. gen., Univ. Louvain*, 1942—1947, 69 (*Chem. Abs.*, 1950, 44, 8315f).

⁴¹ A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 1945, 709.

⁴² 'Heilbron's Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

(Found: C, 70.3; H, 10.9. Calc. for $C_{10}H_{18}O_2$: C, 70.6; H, 10.6%); 5-methoxyoct-3-ene plus 3-methoxyoct-4-ene: *m/e* 142 (M^+ , 1%), 113 (26, $M - C_2H_5$), 99 (100, $M - C_3H_7$), 71 (49), 67 (41), and 45 (16, $CH_2^+O^+Me$); 4,5-dimethoxyoctane: *m/e* 142 ($M - MeOH$, 2%), 113 (7, $M - MeOH - C_2H_5$), 87 (94, $C_3H_7CH=O^+Me$), 57 (16), 55 (28), and 45 (100, $CH_2^+O^+Me$); 2-methoxy-1-propylpentyl acetate: *m/e* 159 ($M - C_3H_7$ and CH_3CO , 1%), 117 (4, $M - C_3H_7 - CH_2CO$), 87 (100, $C_3H_7CH=O^+Me$), 45 (74, $CH_2^+O^+Me$), and 43 (51, CH_3CO^+ and $C_3H_7^+$); and 3- and 5-methoxyoctan-4-one: *m/e* 158 (M^+ , 2%), 126 (8, $M - MeOH$), 97 (57, $M - MeOH - C_2H_5$), 87 (100, $C_3H_7CH=O^+Me$), 83 (42, $M - MeOH - C_3H_7$), 55 (81, $C_4H_7^+$), and 45 (95, $CH_2^+O^+Me$).

Solvolysis of Bromo-octene.—Oct-4-ene (4 g), *N*-bromo-succinimide (6 g), benzoyl peroxide (0.02 g), and carbon tetrachloride (25 ml) were refluxed for 3 h, cooled, and filtered. The precipitate was washed with a small amount of carbon tetrachloride and the solvent removed from the combined liquid phase to give a mixture (4.5 g) of 3-bromo-oct-4-ene and 5-bromo-oct-3-ene; τ 4.05–4.85 (2H, m, CH=CH), 5.25–5.85 (1H, m, CHBr), and 7.6–9.4 (13H, aliphatic envelope). A portion (1.0 g) of this product was shaken with silver acetate (2 g) in acetic acid (10 ml) for 24 h, poured into water, and extracted with ether. Evaporation of the solvent after drying ($MgSO_4$) gave a crude product (0.4 g) which had only one major peak (>97%) on g.l.c. and whose n.m.r. and mass spectra were identical with those of the mixture of 1-propylpent-2-enyl and 1-ethylhex-2-enyl acetates isolated above.

Mercuriation of Styrene.—Mercury(II) acetate (0.6 g)

was added to a solution of redistilled styrene (3.5 g) in water (30 ml) and tetrahydrofuran (30 ml) and stirred for 0.5 h. The clear solution was poured into saturated sodium hydrogen carbonate solution, extracted with dichloromethane, and dried ($MgSO_4$). Removal of the solvent left a pale yellow oil which solidified on cooling. Recrystallisation from chloroform–light petroleum (b.p. 40–60°) gave 2-hydroxy-2-phenylethylmercury(II) acetate (8.2 g, 71%) as white crystals, m.p. 76–79° (lit.,⁴⁷ 76–78°); τ 2.65 (5H, s, ArH), 4.94 (1H, t, *J* 6 Hz, CH), 5.85 (1H, s removed by D_2O , OH), 7.67 (2H, m, non-equiv. CH_2), and 8.09 (3H, s, OAc).

2-Acetoxy-2-phenylethylmercury(II) acetate was similarly obtained, by using acetic acid (previously dried by refluxing for 1 h with a few ml of acetic anhydride) as solvent, as a clear oil which would not solidify; τ 2.76 (5H, s, ArH), 4.09 (1H, t, *J* 6.5 Hz, CH), 7.85 (2H, d, *J* 6.5 Hz, CH_2), and 8.09 and 8.15 (6H, 2 s, OAc). There was no trace of signals at τ 4.94 and 7.67. A portion (4.2 g) of this crude product was mixed with 2M-sodium hydroxide solution (10 ml), and sodium borohydride (0.4 g) in 2M-sodium hydroxide (10 ml) was added. Mercury precipitated immediately but the mixture was shaken a further 0.5 h after which the product was extracted with ether, washed with water, and dried ($MgSO_4$). The solvent was removed and the product analysed in the usual way. A second portion (4.2 g) of the same organomercurial was dissolved in dry dichloromethane (20 ml), sodium borohydride (0.4 g) added, and the mixture shaken. After 0.5 h, water (10 ml) was added and the shaking continued for a further 5 min. The organic layer was separated, washed with sodium hydrogen carbonate, and dried ($MgSO_4$). The solvent was then removed and the product analysed.

We thank the S.R.C. for studentships to A. L. and W. J. E. P.

[4/1608 Received, 1st August, 1974]

⁴⁷ G. Spengler and A. Weber, *Brennstoff-Chem.*, 1959, **40**, 22 (*Chem. Abs.*, 1959, **53**, 19,937i).