

Neighbouring-group Effects in the Oxidation of Olefins by Mercury(II), Thallium(III), and Lead(IV) Acetates

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The participation of neighbouring groups during oxidation of olefins by mercury(II), thallium(III), and lead(IV) acetates has been investigated. With the examples chosen lead(IV) reacts exclusively at the neighbouring group (aryl or phenolic), there being no evidence for electrophilic attack on the double bond. Similarly, mercury(II) is capable of substituting an aromatic ring rather than reacting at an olefinic site; however, the latter reaction can be made to predominate in a more polar medium. The initial ion formed during thallium(III) oxidation is less selective towards nucleophilic attack than the corresponding mercury(II) species, and this is attributed to greater interaction between the metal atom and the positive centre in a mercurio- than in a thallio-cation. Whereas the organo-mercury adducts are stable to the reaction conditions, in thallium(III) oxidations suitable substituents can trap carbocation-like species during both the formation and the destruction of the adducts.

In two recent papers^{1,2} we reported the results of a comparative study of the reactions of mercury(II), thallium(III), and lead(IV) compounds with repre-

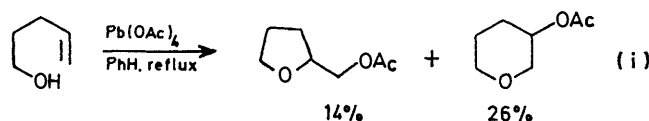
¹ A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1974, 1929.

sentative olefins. We now extend the comparison to olefins in which a neighbouring group is available to react with the carbocations produced in the formation

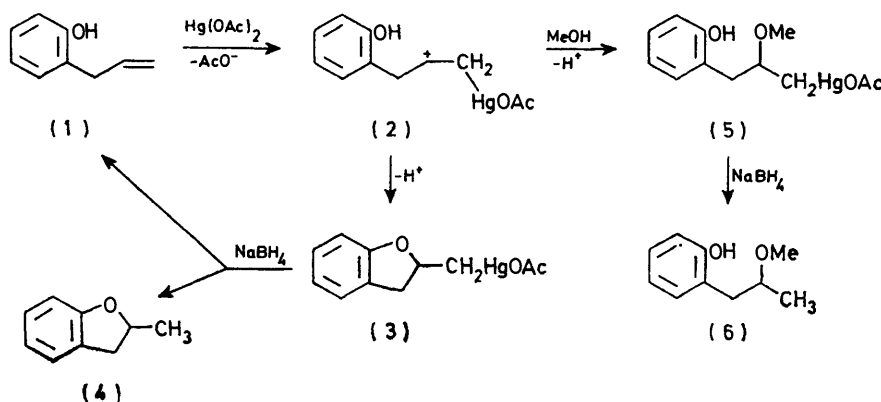
² A. Lethbridge, R. O. C. Norman, C. B. Thomas, and W. J. E. Parr, *J.C.S. Perkin I*, 1975, 231.

and decomposition of the intermediate organometallic adducts. There are a number of examples of substituents trapping such species during the addition of the metal oxidant³⁻⁹ but instances of distant neighbouring groups taking part in the decomposition step are less common. The formation of chroman-3-ols from allyl aryl ethers, however, is probably such a case.¹⁰

A complication to a study of the relative extent of participation of substituents is that, in many cases, the reagent may be able to react not only at the double bond but also with the 'neighbouring group' and the site of primary attack may be difficult to deduce. For instance, the formation of cyclic ethers from unsaturated alcohols on oxidation with lead(IV) acetate^{11,12} [reaction (i)] could involve either nucleophilic attack of the



hydroxy-group on positive centres generated at the double bond site during the formation or decomposition of organolead adducts, or the reaction of an alkoxy radical, the result of homolysis of an alkoxy-lead compound, with the double bond.



SCHEME 1

RESULTS AND DISCUSSION

Oxidation of 2-(Prop-2-enyl)phenol.—Treatment of the phenol (1) with mercury(II) acetate in 1,2-dichloroethane gave 92% of the organomercury compound (3), confirming that the positively charged species* resulting

* For simplicity this species will be considered, for the present, to be the carbocation (2).

† The original report of the reaction of the phenol (1)¹³ claimed that a near-quantitative conversion into the adduct (3) occurred in both aqueous and alcoholic solution. This seems surprising in view of our results in methanol.

³ A. C. Cope, M. A. McKervey, and N. M. Weinshenker, *J. Amer. Chem. Soc.*, 1967, **89**, 2932.

⁴ F. D. Gunstone and R. P. Inglis, *J.C.S. Chem. Comm.*, 1972, 12; L. E. Overman, *ibid.*, 1972, 1196.

⁵ A. McKillop, M. E. Ford, and E. C. Taylor, *J. Org. Chem.*, 1974, **39**, 2434.

⁶ M. Julia and R. Labia, *Bull. Soc. chim. France*, 1972, 4151.

⁷ M. Julia and E. C. Gazquez, *Bull. Soc. chim. France*, 1972, 4148.

from electrophilic attack of mercury(II) on the double bond is quenched by the nucleophilic neighbouring group. Unexpectedly, borohydride reduction of the adduct did not lead to the clean production of 2-methylcoumaran (4); the yield of this compound was only 36%, the major product (62%) being the original olefin.

With methanol as solvent, the adducts (3) and (5) were formed in the ratio 7:12 as judged by n.m.r. spectroscopy; † thus, there is competition between the neighbouring group and the solvent for the carbocation (2). Reduction of the crude product with sodium borohydride led to three products, the olefin (1) (23%), the coumaran (4) (13%), and 2-(2-methoxypropyl)phenol (6) (62%). If the yield of (6) is indicative of that of (5), it follows that adduct formation is, once again, almost quantitative. In neither solvent was there evidence for acetate incorporation.

The regeneration of such a large amount of starting olefin is unusual in the reduction of an organomercurial adduct but is not unique. For example, reduction of the adduct $C_6H_{13}\cdot CH(OAc)\cdot CH_2\cdot HgOAc$ with borohydride leads not only to 1-methylheptyl acetate and octan-2-ol¹⁴ but also to 26% of oct-1-ene^{2,14} (see also ref. 15). The phenoxy- and acetoxy-groups are both characterised by reasonable leaving-group ability, in contrast to more

commonly encountered substituents (HO, MeO, R_2N , etc.) on the β -carbon atom of organomercurials; it is probable that the mercuri-hydride species¹⁶ formed

⁸ J. J. Périé, J. P. Laval, J. Roussel, and A. Lattes, *Tetrahedron*, 1972, **28**, 675.

⁹ H.-J. Kabbe, *Annalen*, 1962, **656**, 204.

¹⁰ J. R. Collier and A. S. Porter, *J.C.S. Chem. Comm.*, 1972, 618.

¹¹ Sung Moon and J. M. Lodge, *J. Org. Chem.*, 1964, **29**, 3453.

¹² M. Lj. Mihailovic, Z. Cekovic, J. Stankovic, N. Pavlovic, S. Konstantinovic, and S. Djokic-Mazinjanin, *Helv. Chim. Acta*, 1973, **56**, 3056.

¹³ R. Adams, F. L. Roman, and W. N. Sperry, *J. Amer. Chem. Soc.*, 1922, **44**, 1781.

¹⁴ A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1973, 2763.

¹⁵ B. Giese, S. Gantert, and A. Schulz, *Tetrahedron Letters*, 1974, 3583.

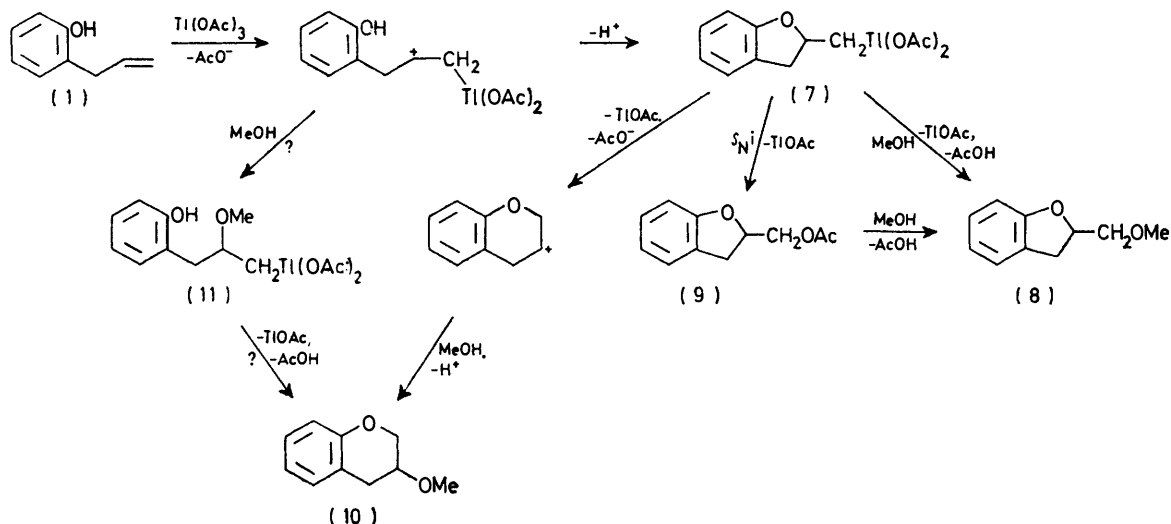
¹⁶ D. J. Pasto and J. A. Gontarz, *J. Amer. Chem. Soc.*, 1969, **91**, 719; C. L. Hill and G. M. Whitesides, *ibid.*, 1974, **96**, 870.

during borohydride reduction readily eliminates Hg^0 , H^+ , and AcO^- or PhO^- .

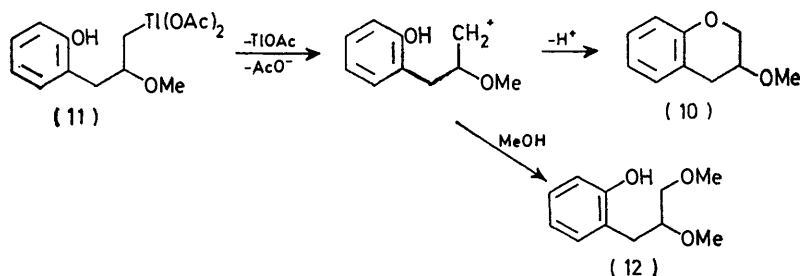
Predictably, thallium(III) acetate oxidation of the phenol (1) gave a more complex spectrum of products than was observed in the mercury(II) reaction. This oxidant is only slightly soluble in methanol at 60 °C, but was rapidly taken into solution when the olefin was added and 4 min after addition only 7% of the alkene remained. From the crude product the thallium adduct (7) was isolated in 55% yield after purification.

Immediately after oxidation the ratio of acetoxy-methylcoumaran to methoxymethylcoumaran is much greater than can be accounted for by competition between acetate ion (or acetic acid) and the solvent for a free carbocation (13). It therefore seems likely that (9) is the product of an $\text{S}_{\text{N}}\text{i}$ decomposition of (7) similar to that proposed previously.¹

In the mercury(II) oxidation solvent (MeOH) attack on the initial carbocation (2) predominates over intramolecular reaction (ratio 1.7 : 1) whereas with thallium,



SCHEME 2

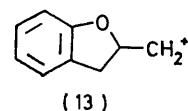


SCHEME 3

Four other products were identified in the mother liquor, namely residual olefin (7%), 2-methoxymethylcoumaran (8) (7%), 2-acetoxymethylcoumaran (9) (7%), and 3-methoxychroman (10) (5%), the last three presumably originating from decomposition of organo-thallium compounds (Scheme 2).

On heating a pure sample of the adduct (7) in methanol for several hours two major products, (8) and (10), were obtained in roughly equal amounts, together with minor quantities of (9). The formation of (10) from (7) is in keeping with our earlier demonstration¹ that substituents on a carbon atom adjacent to a thallium group can migrate during the displacement of that group. An alternative mode of formation of (10), by equilibration of (7) and the uncyclised adduct (11), appears unlikely since no simple 1,2-adducts such as (12) were detected (Scheme 3).

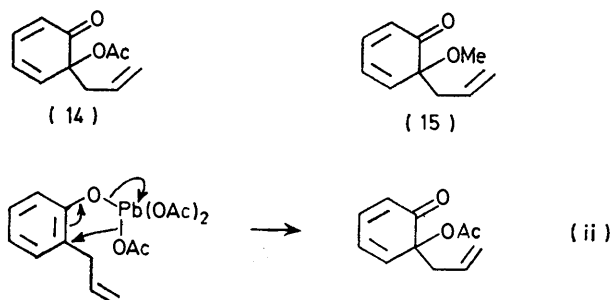
even if it is allowed that (10) arises from (11), the corresponding ratio cannot exceed 0.44 : 1. This indicates that the carbocation formed from the olefin with



mercury(II) is longer lived than that formed with thallium(III), a conclusion which is inconsistent with the representation of such ions as 'free' carbocations. It is likely that there is stabilisation of the positive charge on carbon by interaction with the neighbouring metal atom, this being greater for the more electropositive metal, mercury. There has been a tendency to regard the mercurio-cation produced in electrophilic reactions of

olefins with mercury(II) as a symmetrical species.¹⁷ The high regioselectivity found in solvomercuration of unsymmetrical olefins,^{8,18} however, is more compatible with an unsymmetrical intermediate in which a significant proportion of the charge is carried by the carbon atoms.

Unfortunately with lead(IV) there is no evidence for attack on the double bond. The oxidant reacts rapidly with phenols at room temperature¹⁹ and the only products we were able to identify in the tarry residue obtained on oxidation of (1) in methanol were residual (1) (45%) and the *ortho*-quinol compounds (14) (8%) and (15) (1%). Compound (14) has previously been identified as the major product of oxidation of (1) in acetic acid²⁰ but its formation in the presence of such a large excess of methanol suggests that it cannot result from uptake of acetate (or acetic acid) on a free phenoxy-cation as proposed earlier.²⁰ It is more probably the result of concerted transfer of the acetate from the lead atom [reaction (ii); *cf.* ref. 21]. The lack of reactivity of mercury(II) and thallium(III) towards the phenolic group as compared with lead(IV) is presumably related to the ability of the last oxidant to undergo rapid ligand exchange with molecules possessing hydroxylic groups.¹

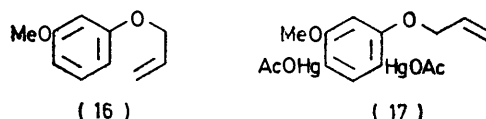


Oxidation of Allyl m-Methoxyphenyl Ether.—We next studied allyl *m*-methoxyphenyl ether (16) since any carbocation generated, be this in the formation or in the decomposition of an adduct, should be capable of substituting into the activated aromatic ring. Oxidation of (16) in 1,2-dichloroethane with mercury(II) acetate led to a 20% recovery of olefin and the isolation of a white amorphous solid, the n.m.r. spectrum and microanalysis of which suggested it to be a dimercuriated aromatic compound [30% yield based on (16)]. The positions of substitution of the aromatic ring were not elucidated but on the basis of the sensitivity of aromatic mercuriation reactions to steric as well as electronic factors²² it is assumed that the compound is (17). In the detailed kinetic investigations of aryl-mercuriation there is no suggestion that aromatic substrates similar to (16) undergo anything other than monosubstitution.²³

¹⁷ W. Kitching, *Organometallic Chem. Rev. (A)*, 1968, **3**, 61; G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, 1973, **95**, 6067.

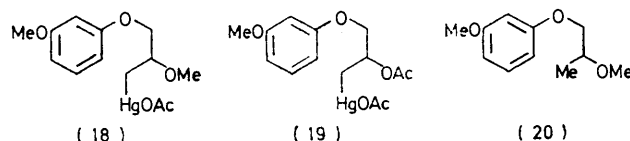
¹⁸ H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, 1969, **91**, 5646; H. C. Brown and J. T. Kurek, *ibid.*, p. 5647; H. C. Brown and P. J. Geoghegan, *J. Org. Chem.*, 1970, **35**, 1844; J. J. Périé and A. Lattes, *Bull. Soc. chim. France*, 1970, 583; D. H. Ballard and A. J. Bloodworth, *J. Chem. Soc. (C)*, 1971, 945; A. J. Bloodworth and G. S. Bylina, *J.C.S. Perkin I*, 1972, 2433; A. J. Bloodworth and R. J. Bunce, *ibid.*, p. 2787.

In contrast, when oxidation was carried out in methanol, the majority of the products originated from



reaction at the double bond. Some (16) was recovered (5%) but three organomercurial compounds (17)—(19), (ratio, from n.m.r. spectroscopy, 2 : 12 : 1) were identified, the last two on the basis of n.m.r. spectra and the products produced on subsequent borohydride reduction. Reduction of the crude product gave unchanged olefin (15%), 2-methoxy-1-(*m*-methoxyphenoxy)propane (20) (57%), and a product tentatively identified as the corresponding acetate (*ca.* 5%), together with *ca.* 7% of the diarylmercury compound mentioned above.

Two points are worthy of note. First, the solvent of higher polarity favours electrophilic attack at the double bond. This is consistent with our knowledge of electrophilic mercuriation at aryl and vinyl sites; the greater delocalisation of the positive charge in a Wheland intermediate than in an unsymmetrical mercurio-cation—and thus in the corresponding transition states—results in the former reaction being less dependent on solvation. Secondly, there is no evidence, from the compounds identified, that the aryl group reacts with the mercurio-cation generated during addition. This is unexpected in view of the susceptibility of *m*-dialkoxybenzenes to electrophilic attack and suggests that such a group is a substantially less effective nucleophile than a phenolic hydroxy-group.



Thallium(III), at first sight, appeared surprisingly unreactive towards (16); after 14 days at 60 °C in 1,2-dichloroethane, a test for thallium(III) was still positive, the olefin was recovered in large amounts, and no products of reaction could be detected by g.l.c. Moreover, whereas under the same conditions in methanol some oxidation products (21)—(25) were detected (yields in all cases <10%), the test still proved positive and much olefin remained unconverted.

Even allowing for thallium(III) reacting with olefins more sluggishly than lead(IV) and mercury(II),¹ oxidation of (16) is still remarkably slow compared with that of

¹⁹ R. Criegee in 'Oxidation in Organic Chemistry. Part A,' ed. K. B. Wiberg, Academic Press, New York, 1965, p. 277.

²⁰ E. Zbiral, W. Wessely, and J. Jörg, *Monatsh.*, 1961, **92**, 654 (*Chem. Abs.*, 1962, **56**, 12784d).

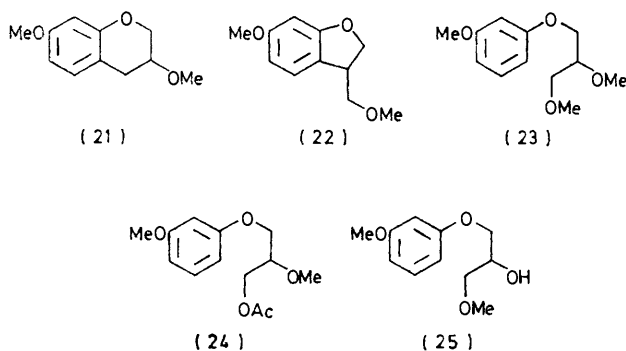
²¹ M. J. Harrison and R. O. C. Norman, *J. Chem. Soc. (C)*, 1970, 728.

²² R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, p. 194.

²³ H. C. Brown and M. Dubeck, *J. Amer. Chem. Soc.*, 1960, **82**, 1939.

similar monosubstituted alkenes. We believe this to be an artefact of competitive metallation (normally an ineffective process²⁴) of the unusually reactive aromatic nucleus. The presence of oxidant, even after 2 weeks, we ascribe to its continual regeneration by protio-dethallation; thallation is known to be a reversible process.²⁵

The oxidation products can be accounted for relatively easily. Compounds (23)—(25) should result from formation and decomposition of an organometallic adduct without the intervention of the neighbouring group;



(25) is a type of product we have never previously obtained from this sort of reaction, but doubtless originates from the water introduced into the system by the use of the sesquihydrate form of thallium(III) acetate. Compound (21) arises from trapping, by the aromatic ring, of the carbocation or incipient carbocation produced on decomposition of the adduct, and (22) is the product of similar capture of the initial thallio-cation. As we found with the allylphenol, nucleophilic attack on the metallo-cation becomes less selective as one goes from mercury to thallium, allowing increased participation by a neighbouring group in the case of the latter reagent. One outstanding point is the apparent discrepancy with the recent report that *para*-substituted allyl phenyl ethers react with thallium(III) sulphate in sulphuric acid to give moderate-to-good yields of chromans.¹⁰ However, this can be reconciled if the reasonable assumption is made that $-\text{Tl}(\text{SO}_4)$ is a better leaving group than $-\text{Tl}(\text{OAc})_2$, thus leading to a greater degree of carbocation character, and hence a lower selectivity, in the decomposition of the adduct with thallium(III) sulphate.

Finally, the arylolefin (16) was oxidised by lead(IV) acetate. Reaction in 1,2-dichloroethane at 60 °C led to

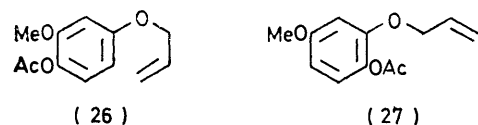
* We found that lead(IV) in methanol alone disappears at a rate consistent with this postulate. However, the kinetic behaviour could not be sensibly analysed. Dissolution of lead(IV) acetate in methanol produces an immediate yellow-ochre colour but the rate of loss of optical density at 380 nm was peculiar. Initially, the optical density rose and then declined in a zero-order manner until the optical density was <25% of its maximum. However, the time taken for destruction of what presumably consists of one or more species $\text{Pb}(\text{OAc})_n(\text{OME})_{4-n}$ varied irreproducibly. It was markedly temperature-dependent (an increase in temperature of 10 °C increased the rate *ca.* 20–30-fold) and was also light-sensitive, characteristics of a radical process. These results are at variance with those of Pocker²⁸ but we could make no sense of our kinetic plots.

consumption of all the lead(IV) in 7 days and the recovery of (16) (29%) together with two nuclear-substituted aryl acetates. Though the substitution pattern of these two compounds was not ascertained unambiguously, they are believed, by analogy with similar systems,²⁶ to be (26) and (27) (24 and 27% yields); the absence of a significant *m/e* 69 ion in their mass spectra is taken as evidence that the three substituents do not occupy adjacent carbon atoms.²⁷ There was no indication of lead(IV) reacting with the double bond.

In view of the effect on the site of attack with the other two oxidants of changing the solvent from 1,2-dichloroethane to methanol, we carried out a reaction in the latter medium but to no avail; the oxidant disappeared completely in 0.5–1.5 h and left a near quantitative amount (88%) of the olefin. Formaldehyde was formed, from which we infer that lead(IV) preferentially oxidises the methanol.²⁸ *

Summary.—The results above extend and complement the comparative study carried out on simple olefins,^{1,2} and they help in the selection of the appropriate oxidant for a particular purpose. The following are the more important features.

(a) The carbocation-like intermediate formed in the addition of the oxidant to the double bond is able to react with any nucleophile present in the system, including a suitably placed substituent in the olefinic



compound; this ion becomes increasingly selective in the series (Pb^{IV}), Tl^{III} , Hg^{II} .

(b) In the second stage of the reaction—decomposition of the organometallic adduct—mercury derivatives are particularly stable. Although the mercury can be displaced with a halogen,^{13,29} the main use of these organomercurials derives from their reduction with borohydride which overall constitutes the addition of HNu to the double bond, where Nu is the nucleophile. However, this process is accompanied in significant proportion by side reactions when the nucleophile is acetic acid or a phenol. The thallium- and lead-containing adducts are much less stable, and there is no evidence that the latter ever survive the reaction conditions; however, the former survive in some cases, and this can lead to unwanted products formed during work-up.¹⁴

²⁴ V. P. Glushkova and K. E. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, 1957, **116**, 233; *Izvest. Akad. Nauk S.S.S.R., Oldel. khim. Nauk*, 1957, 1186, 1391.

²⁵ E. C. Taylor, F. Kienzle, R. L. Robey, A. McKillop, and J. D. Hunt, *J. Amer. Chem. Soc.*, 1971, **93**, 4845; B. Davies and C. B. Thomas, *J.C.S. Perkin I*, 1975, 65.

²⁶ R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1970, 421.

²⁷ C. B. Thomas, *J. Chem. Soc. (B)*, 1970, 430.

²⁸ Y. Pocker and B. C. Davis, *J.C.S. Chem. Comm.*, 1974, 803.

²⁹ G. F. Wright, *J. Amer. Chem. Soc.*, 1935, **57**, 1993; G. Spengler and A. Weber, *Brennstoff-Chemie*, 1959, **40**, 22 (*Chem. Abs.*, 1959, **53**, 19937i).

(c) The facility with which lead(IV) undergoes ligand-exchange ensures that, in hydroxylic solvents, there is little chance of the organo-lead intermediate transferring an acetate ligand from the metal to the adjacent carbon in an S_Ni process, in contrast to the behaviour of thallium-containing adducts; for example, there is a high conversion of oct-1-ene into 1,2-dimethoxyoctane with lead(IV) acetate in methanol, but with thallium(III) acetate the major product is 2-methoxyoctyl acetate.¹

(d) Organo-lead decompositions are almost certainly the most S_N1 -like in character, and this can be utilised in encouraging migration of a suitable substituent (e.g. phenyl³⁰) from the β -carbon atom of the adduct.

(e) Lead(IV) acetate is more prone than the mercury or thallium compounds to oxidise an olefin by other than electrophilic addition, for example by a homolytic process,¹⁹ or by reaction at other functional sites within the molecule.

EXPERIMENTAL

The analytical techniques and a number of the compounds employed in this study have been described previously.^{1,2,14} 1,2-Dichloroethane was distilled from phosphorus pentoxide and stored over sodium hydroxide pellets. 2-(Prop-2-enyl) phenol (Koch-Light) was a commercial sample.

Other Materials.—Allyl *m*-methoxyphenyl ether, prepared by the method of White and Slater,³¹ had b.p. 62° at 0.1 mmHg (lit.,³¹ 73—73.5° at 1 mmHg). 2-Methylcoumaran [from 2-(prop-2-enyl)phenol]³² had b.p. 80° at 12 mmHg (lit.,³² 197° at 740 mmHg). 2-Acetoxyethylcoumaran was obtained from 2-iodomethylcoumaran¹³ by the method of Tinsley³³ and had b.p. 140—145° at 10 mmHg (lit.,³³ 100° at 0.8 mmHg).

2-Methoxymethylcoumaran.—2-Iodomethylcoumaran¹³ (0.5 g) was dissolved in methanol (50 ml) and silver acetate (1 g) added. The mixture was refluxed for 7 days, cooled, filtered, and evaporated. The crude product contained some 2-acetoxyethylcoumaran and was purified by preparative g.l.c. to give 2-methoxymethylcoumaran as a liquid, *m/e* 164 (80%, M^{+}), 133 (12, $M - OMe$), 132 (85, $M - MeOH$), 131 (11, 132 — H), 119 (89, $M - CH_2OMe$), 118 (30), and 91 (100).

2-Acetoxymercuriomethylcoumaran.—2-(Prop-2-enyl)phenol (1.4 g) was added to a stirred suspension of mercury(II) acetate (3.2 g) in dry dichloromethane (20 ml). After 15 min the clear solution was diluted with light petroleum (b.p. 40—60°) and the resultant white solid was recrystallised to give 2-acetoxymercuriomethylcoumaran (4.0 g, 98%) as plates, m.p. 80—81° (from dichloromethane-light petroleum) (lit.,¹³ 80—81°); τ 2.62—3.35 (4H, m, ArH), 4.86 (1H, m, CH), 6.63 (1H, dd, J 15 and 8 Hz) and 7.28 (1 H, dd, J 15 and 6.5 Hz) ($ArCH_2$), 7.74 (2 H, m, CH_2Hg), and 8.05 (3 H, s, OAc).

2-(2-Methoxypropyl)phenol.—2-(Prop-2-enyl)phenol (1.40 g) in methanol (10 ml) was added to mercury(II) acetate (3.18 g) in methanol (10 ml) at room temperature. After shaking for 5 min, the solution was diluted with light petroleum (b.p. 40—60°) and the heavy oil deposited was triturated several times with light petroleum. The n.m.r. spectrum of this oil showed the presence of 2-acetoxy-

mercuriomethylcoumaran and 2-(3-acetoxymercurio-2-methoxypropyl)phenol [τ 6.08 (quintet, $CHOMe$), 6.64 (s, OCH_3), and 7.14 (br d, $2 \times CH_2$)] in the ratio 7:12. To this crude oil was added 3*M*-sodium hydroxide (10 ml) followed by sodium borohydride (0.8 g) in water (10 ml). After 10 min an excess of 2*M*-hydrochloric acid was added, the product was extracted with ether, and the ether solution was extracted with dilute sodium hydroxide. The alkaline layer was acidified and re-extracted with ether, and the extracts were dried ($MgSO_4$) and evaporated. The crude product was carefully distilled to give 2-(2-methoxypropyl)phenol (0.58 g, 33%) as a liquid, b.p. 162° at 50 mmHg; τ 1.52 (1 H, s, OH), 2.7—3.4 (4 H, m, ArH), 6.48 (1 H, m, CH), 6.71 (3 H, s, CH_3), 7.25 (2 H, d, J 5.5 Hz, CH_2), and 8.86 (3 H, d, J 6.5 Hz, CH_3) (Found: C, 72.7; H, 8.5. $C_{10}H_{14}O_2$ requires C, 72.3, H, 8.5%).

2-Diacetoxythalliomethylcoumaran.—2-(Prop-2-enyl)phenol (0.7 g) and thallium(III) acetate (2 g) were heated in dry methanol at 60 °C for 5 min. The solvent was evaporated off and the oily residue taken up into ether. Light petroleum (b.p. 40—60°) was added until a faint cloudiness developed, the mixture was left overnight, and the white precipitate was filtered off. Recrystallisation from chloroform-light petroleum gave 2-diacetoxythalliomethylcoumaran (1.2 g, 52%) as plates, m.p. 110—120° (decomp.) (lit.,⁹ 122°). From the mother liquor of this reaction there was identified, by g.l.c.—mass spectrometry, 3-methoxychroman, *m/e* 164 (100%, M^{+}), 133 (13, $M - CH_3O$), 132 (36, $M - CH_3OH$), 131 (75, $M - CH_3OH - H$), 106 (20, $M - CH_2CH_2OMe$), 91 (52), 78 (44), and 58 (35, CH_2CH_2OMe).

2-Allyl-2-hydroxycyclohexa-3,5-dienone Derivatives.—2-(Prop-2-enyl)phenol (0.7 g) in methanol (10 ml) was added dropwise with stirring to lead(IV) acetate (2.44 g) in methanol (10 ml). The solution was stirred for 30 min and poured into water. The ether extracts were washed with sodium carbonate solution and dried ($MgSO_4$). Removal of the solvent gave a brown-black residue containing considerable unchanged phenol but also 2-allyl-2-methoxycyclohexa-3,5-dienone, *m/e* 164 (100%, M^{+}), 149 (29, $M - Me$), 137 (15, $M - C_2H_5$), 133 (15, $M - OMe$), and 131 (17, $M - Me - H_2O$); and 2-acetoxy-2-allylcyclohexa-3,5-dienone, *m/e* 192 (13%, M^{+}), 150 (54, $M - CH_2CO$), and 109 (100, $M - CH_2CO - C_3H_5$).

Dimercuriated Allyl m-Methoxyphenyl Ether.—Mercury(II) acetate (1.59 g) and allyl *m*-methoxyphenyl ether were warmed at 45 °C in 1,2-dichloroethane (20 ml) for 4 h. The solvent was removed to leave a pale yellow viscous liquid, τ 2.65br (1 H s, ArH), 3.38br (1 H, s, ArH), 3.6—4.3 (1 H, m, =CH), 4.77 (2 H, m, = CH_2), 5.55 (2 H, d, J 5 Hz, CH_2), 6.31 (3 H, s, OCH_3), and 8.02 (6 H, s, OAc). This was taken up in a few ml of ether, added to a saturated solution of potassium bromide, and shaken for 5 min. The resultant white precipitate was recrystallised from hot acetone to give a white amorphous solid decomposing above 150°, believed to be 1-allyloxy-2,4-bis(bromomercurio)-5-methoxybenzene; τ similar to the compound above except for the absence of OAc signals (Found: C, 15.8; H, 1.4. $C_{12}H_{10}Br_2Hg_2O_2$ requires C, 16.6; H, 1.4%).

Reduction with sodium borohydride of a sample of the pale yellow viscous oil gave a grey oil which, when taken up in a mixture of dichloromethane and light petroleum

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³¹ W. N. White and C. D. Slater, *J. Org. Chem.*, 1961, **26**, 3631.

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³³ S. W. Tinsley, *J. Org. Chem.*, 1959, **24**, 1197.

(b.p. 40–60°), gave a white solid, m.p. 75–78°; τ 2.5–3.6 (m, ArH), 3.5–5.0 (m, CH=CH₂), 5.45 (d, CH₂), and 6.21 (s, OCH₃).

1-Acetoxymercurio-2-methoxy-3-(*m*-methoxyphenoxy)propane.—A pale brown viscous oil was obtained by subjecting allyl *m*-methoxyphenyl ether to the mercury(II) acetate-methanol treatment detailed above. N.m.r. spectroscopy showed the main component to be 1-acetoxymercurio-2-methoxy-3-(*m*-methoxyphenoxy)propane, τ 2.55–3.55 (4 H, m, ArH), 5.8–6.35 (m, O·CH₂·CH) and 6.23 (s, ArOCH₃) (total 6 H), 6.60 (3 H, s, CH·OCH₃), and 7.7–8.1 (m, CH₂Hg) and 7.99 (s, OAc) (total 5 H). Recrystallisation of this oil proved impossible and the crude product was reduced directly with sodium borohydride solution as described above. From the reduction product was isolated, by preparative g.l.c., 2-methoxy-1-(*m*-methoxyphenoxy)propane, τ 2.65–3.65 (4 H, m, ArH), 5.9–6.5 (m, O·CH₂·CH) and 6.26 (s, ArOCH₃) and 6.60 (s, CH·OCH₃) (total 9 H), and 8.76 (3 H, d, *J* 6 Hz, CH·CH₃); *m/e* 196 (30%, *M*⁺), 125 (41), 124 [30, *M* – CH₂=C(OMe)Me], 73 [32, CH₂·CH(OMe)Me], 72 [15, CH₂=C(OMe)Me], and 59 (100, MeCH=OMe).

Products of Oxidation of Allyl *m*-Methoxyphenyl Ether by Thallium(III) Acetate.—Thallium(III) acetate (1.02 g) and allyl *m*-methoxyphenyl ether (0.41 g) were heated under reflux in dry methanol (10 ml) for 14 days. The solution was poured into ice-water, left for ½ h, and extracted with ether; the extracts were dried and the solvent removed. G.l.c.-mass spectrometry on the residual oil showed the presence of four major products: 3,7-dimethoxychroman, *m/e* 194 (79%, *M*⁺), 162 (24, *M* – MeOH), 161 (25, *M* – MeOH – H), 136 (100, *M* – CH₂=CH·OMe), 108 (58, 136 – CO), 79 (12, C₆H₇⁺), 78 (22, C₆H₈⁺), and 77 (14, C₆H₅⁺); 1,2-dimethoxy-3-(*m*-methoxyphenoxy)propane, *m/e* 226 (47%, *M*⁺), 194 (9, *M* – MeOH), 149 (30, *M* – MeOH – CH₂OMe), 125 (36, *M* – C₅H₉O₂), 124 (38, *M* – C₅H₁₀O₂), 102 [39, CH₂=C(OMe)·CH₂OMe], 71 (49), 59 (20), and 45 (100, CH₂=OMe); 1-methoxy-3-(*m*-methoxyphenoxy)propan-2-ol, *m/e* 212 (48, *M*⁺), 149 (22, *M* – H₂O – CH₂OMe), 125 (69, *M* – C₄H₉O₂), 124 (100, *M* – C₄H₈O₂), 75 (29, MeO·CH₂·CH=OH), and 45 (45, MeO=CH₂); 2-

methoxy-3-(*m*-methoxyphenoxy)propyl acetate, *m/e* 254 (22%, *M*⁺), 212 (11, *M* – CH₂CO), 149 (17, *M* – AcOCH₂ – MeOH), 138 (16, *M* – MeOCH=CHOAc), 131 (52, C₆H₁₁O₃), 125 (36, *M* – C₆H₉O₃), 124 (61, *M* – C₆H₁₀O₃), 71 (61), and 43 (100, CH₃C=O).

Allyloxymethoxyphenyl Acetates.—A solution of allyl *m*-methoxyphenyl ether (0.82 g) and lead(IV) acetate (2.44 g) in 1,2-dichloroethane (20 ml) was heated at 40 °C for 157 h. The mixture was poured into water, and the organic layer was washed with dilute sodium carbonate solution and dried (MgSO₄). After removing the solvent the residual oil was subjected to g.l.c. and mass spectrometric analysis. Two major products were obtained which are believed to be 4-allyloxy-2-methoxyphenyl acetate and 2-allyloxy-4-methoxyphenyl acetate: *m/e* (first product) 222 (22% *M*⁺), 180 (77, *M* – CH₂CO), 139 (100, *M* – CH₂CO – CH₂=CH·CH₂), 111 (25, 139 – CO), and 69 (2, C₄H₅O); *m/e* (second product) 222 (19%, *M*⁺), 180 (79, *M* – CH₂CO), 139 (100, *M* – CH₂CO – CH₂=CH·CH₂), 111 (15, 139 – CO), and 69 (4, C₄H₅O⁺).

***p*-Tolylthallium Diacetate.** Thallium(III) acetate (3.2 g) and toluene (15 ml) were refluxed for 20 h. After cooling, and concentrating to half-volume, the white precipitate was filtered off to give *p*-tolylthallium diacetate, m.p. 168–172° (decomp.) (from benzene); τ [(CD₃)₂SO] 2.57br (2 H, d, *J*_{TH}, 878 Hz, ArH adj. to Tl), 2.79br (2 H, d, *J*_{TH} 301 Hz, ArH adj. to CH₃), ca. 6.97br (3 H, d, *J*_{TH} 59 Hz, CH₃), and 8.13 (6 H, s, OAc) (Found: C, 31.0; H, 2.9. C₁₁H₁₃O₄Tl requires C, 31.9; H, 3.2%).

Oxidations.—The general procedure was the same as that detailed previously,¹ reaction being assumed complete when the usual tests for the oxidants¹ employed proved negative.

Decomposition of Lead(IV) Acetate in Methanol.—Lead(IV) acetate (88.9 mg) was dissolved in methanol (100 ml) and some of the solution was immediately transferred to the cell compartment of a Unicam SP 800 spectrometer thermostatted at 30 °C. The optical density of the solution at 380 nm was determined every 32 s until it reached a constant value.

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