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# Reactions of Lead Tetra-acetate. Part XV.<sup>1</sup> The Oxidation of $\alpha$ - and *cis*- and *trans*- $\beta$ -Methylstyrene

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Like styrene,  $\alpha$ -methylstyrene and *cis*- and *trans*- $\beta$ -methylstyrene are oxidised by lead tetra-acetate by concurrent homolytic and heterolytic pathways. The relative significance of the two types of reaction is dependent on the conditions. For  $\alpha$ -methylstyrene, the relative importance of the homolytic reaction is much smaller than for styrene, at least in part because the heterolytic reaction is so much faster ( $k_{rel.} = 19$ ), whereas for the  $\beta$ -methylstyrenes both types of reaction are much slower than for styrene. The heterolytic reaction occurs by way of an adduct for which there are competitive reaction paths, namely, the migration of the phenyl group and the formation of an acetoxonium ion; for  $\alpha$ -methylstyrene, the former dominates whereas, for the  $\beta$ -methylstyrenes, products to be expected from phenyl-migration could not be detected, and an explanation for this difference is suggested. The acetoxonium ion can be opened by reaction with water to give hydroxyacetates, and this has enabled the stereo-chemistry of the heterolytic reactions of the  $\beta$ -methylstyrenes with lead tetra-acetate to be studied; the results are compared with those for oxidation by the ' wet' Prévost procedure. Autoxidation is catalysed under the reaction conditions, and gives hydroxyacetates and the aromatic carbonyl compounds formed by cleavage of the olefinic bond.

WE have previously shown that the oxidation of styrene by lead tetra-acetate occurs simultaneously by homolytic and heterolytic pathways.<sup>2</sup> The former involves a chain reaction in which the propagation steps are thought to be (a) the addition of a methyl radical, probably derived from  $\cdot$ Pb(OAc)<sub>3</sub>, to the terminal carbon atom of styrene, and (b) oxidation of the resulting radical by a molecule of lead tetra-acetate to give the corresponding carbonium

<sup>1</sup> Part XIV, R. O. C. Norman and M. Poustie, J. Chem. Soc. (B), 1968, 781.

ion, and thence the adduct  $PhCH(OAc)CH_2CH_3$  (I), and the chain-carrying species,  $\cdot Pb(OAc)_3$ . The heterolytic pathway is thought to involve the organolead(IV) intermediate (II) which undergoes heterolysis of the C-Pb bond either with migration of the phenyl group to give ultimately the 1,1-diacetate (III) or with participation of the acetate group to give the cyclic acetoxonium ion and thence the 1,2-diacetate (IV). There is also evidence

<sup>2</sup> R. O. C. Norman and C. B. Thomas, J. Chem. Soc. (B), 1967, 771.

that some of the 1,2-diacetate is formed by a homolytic mechanism.2

$$\begin{array}{c|cccc} \operatorname{PhCH-CH}_2 & \operatorname{PhCH-CH}_2 & \operatorname{PhCH-CH}_2 \\ & & & & & \\ \operatorname{AcO} & \operatorname{Pb(OAc)}_3 & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

We have now extended our study to the oxidation of  $\alpha$ -methylstyrene and *cis*- and *trans*- $\beta$ -methylstyrene with the aim of both delineating the scope of the homolytic mechanism and determining, from the behaviour of the  $\beta$ -methylstyrenes, the stereochemistry of the heterolytic reaction leading to 1,2-diacetates.

Products from the Oxidation of  $\alpha$ -Methylstyrene.—The oxidation of  $\alpha$ -methylstyrene (V) by lead tetra-acetate has been cursorily examined by Hock and Kropf in connection with the reaction of  $\alpha$ -cumyl hydroperoxide with this oxidant; 3 they reported the formation of benzyl methyl ketone (VI) and the hydroxyacetate (VII), and assumed that the latter was produced by partial hydrolysis of the diacetate. We employed the general procedure previously employed for the oxidation of styrene<sup>2</sup> and found that six products are formed under all the conditions we used. Five of these were identified, by comparison with authentic materials, as benzyl methyl ketone, the hydroxyacetate (VII), the allylic acetate (VIII), the acetoxyketone (IX), and acetophenone (XIII). The hydroxyacetate (VII) was prepared by the 'wet' Prévost oxidation of a-methylstyrene, and evidence that both this product and that from the lead tetra-acetate oxidation were the 1-acetate of 2-phenylpropane-1,2-diol and not the isomeric 2acetate (which could not be ruled out on the basis of the previous evidence<sup>3</sup>) was derived from the n.m.r. spectrum; the methyl resonance of the hydroxyacetate  $(\tau 8.47)$  was much closer to that in the diol  $(\tau 8.54)$  than to that in the diacetate  $(\tau 8.11)$ , whereas for the methylene resonance ( $\tau$  5.80) the opposite was the case [diol,  $\tau$  6.44 (centre of an AB system); diacetate,  $\tau 5.64$ ].

Gas chromatography showed that the sixth product was relatively unstable; as the chromatography temperature was increased from 140°, the peak due to the compound developed an increasingly mis-shapen leading edge, and when a sample was eluted from the chromatograph into a mass spectrometer via a superheated stainless-steel capillary the spectrum closely resembled in its major peaks that from benzyl methyl ketone. When the temperature of the capillary was reduced to that of the chromatograph, the spectrum obtained was consistent with the compound's being benzyl methyl ketone diacetate (X), which would be expected to break down fairly readily to the ketone. [There is little systematic

information about the stability of ketone diacetates. Those from benzophenone and fluorenone are reported as crystalline compounds with sharp m.p.s,<sup>4</sup> and others are claimed to be isolable by distillation.<sup>5</sup> Acetone, cyclopentanone, and cyclohexanone are reported to give stable diacetates, whereas methyl propyl ketone apparently does not.<sup>6</sup> In other cases, there is i.r. evidence for the formation of diacetates, but on attempted isolation they have been found to decompose to the ketone,<sup>7</sup> and in some instances, where the diacetate has been expected, only the ketone has been found.<sup>8</sup>] Although there was no peak at m/e 226 (mass peak for benzyl methyl ketone diacetate), there was a significant peak at m/e 176 (M – HOAc) and a base peak at m/e 134. The latter may be produced in part by the loss of keten from the ion which gives the m/e 176 peak (metastable at 102.0), and can be represented as (PhCH=CMeOH)<sup>+\*</sup>. [A contribution to this peak might be made by (PhCH<sub>2</sub>·COMe)<sup>+•</sup> (produced from the diacetate by either fragmentation on electron impact or partial pyrolysis in the stainless-steel capillary), but this cannot be the major contributor since the mass spectrum from benzyl methyl ketone has a base peak at m/e 43 and a very strong peak at m/e 91, whereas both these peaks, though present, were much weaker than that at m/e 134. In the spectrum from benzyl methyl ketone there is no metastable peak at m/e 61.8 corresponding to the transition  $134 \rightarrow 91$ , so that it is probable that the m/e 91 fragment is not formed directly from the molecular ion, as was originally thought,<sup>9</sup> but results from  $\alpha$ -cleavage to give the ion with m/e 119 (PhCH<sub>2</sub>CO<sup>+</sup>) followed by loss of CO. The occurrence of a weak peak at m/e 119, and a metastable peak at m/e 105.7 for the transition  $134 \rightarrow 119$ , is consistent with this view, although no metastable peak was observed for the transition  $119 \rightarrow 91$ .] Other major peaks were at m/e 117 (loss of OH from the major fragment of m/e 134; metastable at 102.1), 116 (probably a fragment derived by loss of HOAc from that at m/e 176; no metastable observed), 115 [derived partially by loss of H from the preceding fragment (metastable at 114.0), and partially by loss of  $H_2$  from the fragment giving m/e 117 (metastable at 113.0)], 105, 103, and 77. An attempt to make the diacetate from the ketone, by a modification of the method for aldehyde 1,1-diacetates,<sup>10</sup> was only partially successful; the product, though consisting largely of unchanged ketone, contained a component whose n.m.r. spectrum was in accord with its being the ketone diacetate (resonances at  $\tau$  6.56, 8.01, and 8.18, in the approximate ratio 2:6:3; cf. the resonances for benzyl methyl ketone at  $\tau$  6.34 and 7.92), but attempts to isolate it were unsuccessful. The gas chromatogram from this preparation contained a peak with the same

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

9 H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, Inc., San

<sup>&</sup>lt;sup>3</sup> H. Hock and H. Kropf, Chem. Ber., 1958, 91, 1681.

<sup>&</sup>lt;sup>4</sup> H. R. Hensel, Chem. Ber., 1955, 88, 527.

<sup>&</sup>lt;sup>5</sup> J. Jadot and M. Neuray, Bull. Soc. roy. Sci. Liège, 1961, 30, 34, 431.

 <sup>&</sup>lt;sup>6</sup> I. V. Machinskaya, V. A. Barkhash, and V. I. Molchanov, *Zhur. obshchei Khim.*, 1953, 23, 756.
 <sup>7</sup> J. J. Tufariello and W. J. Kissel, *Tetrahedron Letters*, 1966, 6145; W. J. Koehl, *J. Org. Chem.*, 1967, 32, 614.

Francisco, 1967, p. 168.
 <sup>10</sup> E. H. Man, J. J. Sanderson, and C. R. Hauser, J. Amer. Chem. Soc., 1950, 72, 847.

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retention time as that of the sixth product from the lead tetra-acetate oxidations, and the n.m.r. resonances were also present in the crude products from these oxidations, reinforcing our conclusion that the sixth product was the ketone diacetate (X).

Two other products, formed under some of the conditions we used, were identified by comparison with the authentic materials as the adduct (XI) of  $\alpha$ -methylstyrene and a methyl and an acetoxy-group and the 1,2-diacetate (XII). The results are in Table 1. In as for styrene <sup>2</sup> gave four products which were identified, by comparison with authentic materials, as the adduct (XVI), the diastereoisomeric diacetates (XVII) and (XVIII), and benzaldehyde (XIX). A fifth peak on the gas chromatogram had a retention time consistent with its being due to either or both of the hydroxyacetates (XX) and (XXI), and when the crude products were acetylated this peak was removed and those corresponding to the diacetates (XVII) and (XVIII) were increased; the proportions of the *threo* and *erytho*-isomers in the

TABLE .
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Distribution of products from the oxidation of  $\alpha$ -methylstyrene by lead tetra-acetate in acetic acid (except where stated)

		Time	Products (%)								
Expt.	Temp.	(hr.)	$\overline{(V)}$	(VI)	(VII)	(VIII)	(IX)	(X) a	(XI)	(XII)	(XIII)
ī	45°	1.5	0.9	41	15	4.4	4.8	27			0.4
2	60	0.5	$3 \cdot 2$	40	18	4.1	4.7	20			0.4
3	80	0.25	7.1	40	14	4.7	4.5	17	$2 \cdot 8$	1.1	0.4
4	60	18	1.1	46	12	4.7	$4 \cdot 2$	0.8		$5 \cdot 1$	1.8
50	60	0.2	0.8	<b>25</b>	19	$2 \cdot 6$	3.1	15	12	6.6	1.4
6 °	80	4	<b>26</b>	12	3.6	11	<b>4</b> ·8	21	$5 \cdot 3$		1.2

• Approximate value; since no authentic sample of (X) could be obtained, it was assumed that the sensitivity of the compound to the gas-chromatographic detector was the same as that of the isomeric diacetate (XII). <sup>b</sup> In the presence of di-isopropyl peroxydicarbonate (Perkadox) (50 mg.). • In benzene under reflux.

TABLE 2 Distribution of products from the oxidation of *trans*- $\beta$ -methylstyrene by lead tetra-acetate in acetic acid (except where stated)

		Time	Products (%)						Ratio #	
Expt.	Temp.	(hr.)	(XIV)	(XVI)	(XVII)	(XVIII)	(XIX)	(XX) + (XXI)	(XVII) : (XVIII)	
7	60°	16	0.4	3.7	10	9	11	25	67:33	
8	80	4	14	9	18	11	7	11	71:29	
9,	60	3	1.6	10	<b>23</b>	18	5	25	62:38	
10 °	80	6	14	3.4	<b>23</b>	9	9	17	65:35	
11 ª	80	48	22	13	20	12	1.9	Trace		
12•	60	48	<b>24</b>	4.1	23	8	$2 \cdot 5$	1.6		
13 °	80	10	29	6	19	7	1.3	Trace		
14 e, f	80	10	15	7	21	9	$1 \cdot 2$	10	85:15	
15 e,g	80	5	15	16	18	10	1.7	1.3		

<sup>6</sup> From acetylation of the hydroxyacetates (XX) + (XXI). <sup>b</sup> In the presence of di-isopropyl peroxydicarbonate (50 mg.). <sup>c</sup> In the presence of *p*-benzoquinone (50 mg.). <sup>d</sup> In benzene. <sup>e</sup> Under nitrogen. <sup>f</sup> In the presence of 1 mol. of water. <sup>e</sup> In the presence of 1 mol. of sodium acetate.

addition,  $\alpha$ -methylstyrene was oxidised by iodine in glacial acetic acid containing a small quantity of water and suspended silver acetate<sup>11</sup> (the 'wet' Prévost reaction) to give, after acetylation, benzyl methyl ketone (5.6%), the allylic acetate (VIII) (20%), the 1,2-diacetate (XII) (62%), and acetophenone (2.1%).

$$\begin{array}{c|cccccccc} PhMeC-CH_2 & Ph & PhCH-COMe \\ & & C-CH_2OAc & \\ OH OAc & CH_2 & OAc \\ (VII) & (VIII) & (IX) \\ OAc & \\ & OAc \end{array}$$

$$\begin{array}{cccccc} PhCH_2 & -\dot{C} - Me & PhMeC - CH_2Me & PhMeC - CH_2\\ & & & & & & \\ OAc & OAc & AcO OAc\\ (X) & (XI) & (XII) \end{array}$$

Products from the Oxidation of cis- and trans- $\beta$ -Methylstyrene.—Oxidation of each olefin by lead tetra-acetate hydroxyacetates were then determined from the gas chromatograms obtained before and after acetylation of the crude product. Two unidentified materials (ca. 5%) were formed under most conditions: one was formed from both cis- and trans- $\beta$ -methylstyrene (as judged by its retention time on gas chromatography), and the other, which was not common to both olefins, had a retention time in the range expected for the respective olefin oxides (see the later discussion of autoxidation).

The results for the oxidations of *trans*- $\beta$ -methylstyrene (XIV) and its *cis*-isomer (XV) are in Tables 2 and 3.

The olefins were also submitted to the 'wet' Prévost oxidation, followed by acetylation of the crude product. Both gave the diastereoisomeric diacetates (XVII) and (XVIII) and benzaldehyde (analysed as benzylidene diacetate) in yields, respectively, of 16, 71, and 1.4%

<sup>11</sup> K. B. Wiberg and K. A. Saegebarth, J. Amer. Chem. Soc., 1957, 79, 6256.

from the *cis*-olefin and 82, 7, and 1.8% from the *trans*isomer.



Kinetics of Oxidation of  $\alpha$ -Methylstyrene and trans- $\beta$ -Methylstyrene by Lead Tetra-acetate.—The rate of consumption of lead tetra-acetate in the presence of each of these olefins in acetic acid at 60° was measured by following the change in the optical density at 360 nm.

actions occur much more rapidly on a-methylstyrene than on styrene; thus, at 60° in acetic acid, the secondorder rate constant for reaction of the former olefin is 19 times that for the latter, and we presume that the former rate constant, like the latter,<sup>2</sup> refers to a heterolytic reaction. Thus, there is no indication that the homolytic reaction is any slower for  $\alpha$ -methylstyrene than for styrene, and comparison of the data from experiments 2 and 5 with those for styrene shows that the homolytic process is associated with propagating chains of similar length for the two olefins. As with styrene, the yield of (XI) was increased by increase in the temperature when acetic acid was the solvent and was larger in benzene than in acetic acid at 80°.

Under all conditions, the major product was benzyl methyl ketone, either as such or as its diacetate precursor (X). The formation of this compound is consistent with the mechanism suggested by Criegee for the

TABLE 3

Distribution of products from the oxidation of cis- $\beta$ -methylstyrene by lead tetra-acetate in acetic acid

		Time		Ratio <sup>a</sup>					
Expt.	Temp.	(hr.)	(XV)	(XVI)	(XVII)	(XVIII)	(XIX)	(XX) + (XXI)	(XVII) : (XVIII)
16	60°	21	12	0.7	13	10	17	16	38:62
17 0	60	4	<b>21</b>	8	15	13	8	9	45:55
18 °	80	13	17	9	33	15	0.4		
19 c, d	80	14	12	10	27	16	0.9	10	31:69
a T		. ( . 1 1	1		(XXXXX) h	Tu the mass	man of d:	iconnonul nonourd	icarbonata (50 mg)

<sup>a</sup> From acetylation of the hydroxyacetates (XX) + (XXI). <sup>b</sup> In the presence of di-isopropyl peroxydicarbonate (50 mg.). <sup>c</sup> Under nitrogen. <sup>d</sup> In the presence of 1 mol. of water.

with solutions which were 0.016M in each reagent.  $\alpha$ -Methylstyrene gave a second-order plot for more than 70% of the reaction; the derived rate constant was 153 l. mole<sup>-1</sup> hr.<sup>-1</sup>. With *trans*- $\beta$ -methylstyrene secondorder kinetics were followed for ca. 24 hr., during which less than 10% of the oxidant was consumed (k = ca. 0.12 l. mole<sup>-1</sup> hr.<sup>-1</sup>), but thereafter the rate increased considerably and the kinetics approximated to zero order. When the initial concentration of trans- $\beta$ methylstyrene was increased to 0.032 and then 0.048M, the period during which the slow, second-order reaction occurred was reduced to ca. 11 and 4 hr., respectively.

Mechanism of Oxidation of  $\alpha$ -Methylstyrene by Lead Tetra-acetate.-The product (XI) which is formally derived by the addition of a methyl and an acetoxygroup to the double bond of α-methylstyrene was formed in low yield under some of the conditions we employed. We infer that (XI) results from a homolytic reaction sequence similar to that which occurs in the conversion of styrene into the adduct, PhCH(OAc)Et; moreover, (XI) was formed in 12% yield in acetic acid at  $60^{\circ}$  when the radical-initiating species, Perkadox, was added in catalytic quantities whereas it was not produced in detectable yield under these conditions when the catalyst was omitted (cf. expts. 2 and 5). For the same conditions, the yield of (XI) from  $\alpha$ -methylstyrene was in all cases considerably lower than that of the analogue from styrene, but this is evidently because alternative re-

<sup>12</sup> R. Criegee, in 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Part A, Academic Press, 1965, ch. 5.

oxidative rearrangement of p-methoxystyrene and some related compounds; 12 and the greater rate of reaction of  $\alpha$ -methylstyrene than styrene is consistent with initial addition of the electrophilic lead species to give the adduct (XXIII) by way of <sup>13</sup> the carbonium ion (XXII) (Scheme 1). The enol acetate, MeC(OAc)=CHPh, which could be formed by loss of a proton from the intermediate carbonium ion (XXIV), was not detected; evidently the preferred reaction for this ion is with acetate ion or acetic acid to give the 1,1-diacetate (X).

When benzyl methyl ketone was oxidised by lead tetraacetate under the conditions of experiment 2, only 2.7%of the acetoxyketone (IX) was isolated, together with 94% of unchanged ketone. This route cannot apparently account for all the acetoxyketone (IX) formed from  $\alpha$ methylstyrene under the conditions of experiment 2, although it is possible that the reactivity of lead tetraacetate as an oxidant for the ketone is enhanced, in the presence of  $\alpha$ -methylstyrene, by complex-formation between oxidant and olefin (cf. refs. 13, 14).

The possibility that the hydroxyacetate (VII) is formed by partial hydrolysis of the 1,2-diacetate (XII), as previously suggested,<sup>3</sup> is discounted by our finding that this diacetate is stable under conditions which are more severe than those used for the oxidation of  $\alpha$ methylstyrene; thus, when the diacetate was heated at  $80^{\circ}$  in acetic acid for 2 hr., it was recovered in 93% yield

<sup>&</sup>lt;sup>13</sup> R. O. C. Norman and C. B. Thomas, J. Chem. Soc. (B), 1967, 604. <sup>14</sup> J. D. Bacha and J. K. Kochi, Tetrahedron, 1968, 24, 2215.

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and there was no trace of other products. It is likely that the hydroxyacetate results from the reaction of water with the acetoxonium ion (XXV) in a manner analogous to that in the 'wet' Prévost reaction. The amount of water necessary to give a 20% yield of the hydroxyacetate is only 36 mg., corresponding to a concentration of 0.28% water in the acetic acid used. This was an analytical reagent whose hydroxyl resonance in the n.m.r. spectrum was at  $\tau - 1.49$ , indicating it to be essentially dry,<sup>15</sup> but after a 13 ml. sample had been stirred at  $60^{\circ}$  for 30 min. in the apparatus used for the oxidations, including a silica-gel guard tube to protect against water from the atmosphere, the hydroxyl resonance was at  $\tau$  -1.27, corresponding to a water content of  $0.50 \pm 0.03\%$ . The water taken up is likely to come from moist air trapped within the apparatus rather than from the outside atmosphere via the

by a homolytic mechanism. Secondly, the ca. 5% yield of the diacetate under the conditions of experiment 4 must arise by acetylation of the hydroxyacetate (VII) and not by oxidation, for the lead tetra-acetate is completely consumed in 0.5 hr. under these conditions, at which time no diacetate is detectable (expt. 2), and the yield of the hydroxyacetate is correspondingly reduced during the remaining reaction time.

The identification of the hydroxyacetate (VII) as a product of the oxidation of  $\alpha$ -methylstyrene by lead tetra-acetate suggested that hydroxyacetates might also be formed in the corresponding oxidation of styrene. This proved to be so; a mixture of the hydroxyacetates (XXVII) and (XXVIII) was shown to be present by comparison of the n.m.r. spectrum and gas chromatographs of the oxidation product with those of an authentic mixture of the compounds, and the appropriate



guard tube because when, in the above control experiment, acetic acid was replaced by benzene containing lead tetra-acetate, the precipitation of lead dioxide stopped after a short time.

The allylic acetate (VIII) might be formed either from the acetoxonium ion (XXV) by loss of a proton (Scheme I) or from the carbonium ion (XXII) by the sequence  $(XXII) \longrightarrow CH_2 = CPh - CH_2 - Pb(OAc)_3 \longrightarrow$  $CH_2=CPh-CH_2OAc + Pb(OAc)_2$ . The formation of this product in relatively high yield from  $\alpha$ -methylstyrene by the 'wet' Prévost procedure suggests that the former path is the more likely.

A possible path to the 1,2-diacetate (XII) would be by reaction of the acetoxonium ion (XXV) with acetate ion or acetic acid, but this is unlikely for the following reasons. First, at  $60^{\circ}$  in acetic acid, ca. 7% of the 1,2diacetate was formed in the presence of Perkadox whereas none was detected in its absence (expts. 2 and 5); under these conditions, the diacetate is evidently formed

15 L. W. Reeves and W. G. Schneider, Trans. Faraday Soc., 1958, 54, 314.

n.m.r. resonances and gas-chromatographic peak (which was previously unidentified<sup>2</sup>) were removed after acetylation of the oxidation product. [The isomers (XXVII) and (XXVIII) undergo interconversion even at room temperature. Cohen et al.<sup>16</sup> found that, after  $4\frac{1}{2}$  weeks, (XXVIII) gives a mixture of (XXVII) and (XXVIII) in the ratio 1.8:1, and when we attempted to prepare (XXVII) by the reduction of phenacyl acetate we obtained a mixture in the ratio 2.5:1 (n.m.r. spectrum). The 'wet' Prévost reaction gave the same mixture. Interconversion presumably <sup>17</sup> occurs by way of the ortho-ester corresponding to (XXVI). We should expect equilibrium to be established in a similar manner between the hydroxyacetate (VII) and its isomer, PhMeC(OAc)·CH<sub>2</sub>OH, so that our failure to detect the latter compound on oxidation of *a*-methylstyrene by lead tetra-acetate or the 'wet' Prévost procedure suggests that equilibrium is strongly in favour of the former

<sup>16</sup> T. Cohen, M. Dughi, V. A. Notaro, and G. Pinkus, J. Org.

Chem., 1962, 27, 814. <sup>17</sup> C. B. Anderson, E. C. Friedrich, and S. Winstein, Tetrahedron Letters, 1963, 2037.

isomer.] We therefore examined the oxidation of styrene by lead tetra-acetate in the presence of one equivalent of water, thereby ensuring that the acetoxonium ion would give hydroxyacetates and no diacetate, and determined the yields of the hydroxyacetates (XXVII) and (XXVIII) as well as <sup>2</sup> PhCH(OAc)·CH<sub>2</sub>Me (I), PhCH<sub>2</sub>·CH(OAc)<sub>2</sub> (III), PhCH(OAc)·CH<sub>2</sub>OAc (IV), and benzaldehyde (XIX) (Table 4). Two features of the results are notable. First, none of the adduct (I) which characterises the homolytic reaction was formed under the conditions of experiment 20, so that the 1,2diacetate (IV) is evidently formed under these conditions by a heterolytic pathway. Secondly, under conditions which favour the homolytic reaction  $(80^{\circ})$ , the addition of an inhibitor brings about a five-fold decrease in the yield of the 1,2-diacetate (IV) (compare expts. 21 and 22), indicating that in these circumstances (IV) results largely from a homolytic reaction. Since the yield of the adduct (I) is reduced 20-fold by the inhibitor, a fraction of the diacetate is apparently formed by a heterolytic reaction, possibly via the hydroxyacetates (this could account for ca. 0.8% of the 1.2% yield of the diacetate in experiment 22; see the final paragraph of the Discussion section).



#### TABLE 4

Distribution of products from the oxidation of styrene by lead tetra-acetate (expts. 20-22) and by iodinesilver acetate (expt. 23) in wet acetic acid

			Products (%)					
Expt. 20 21 22 a 23 b	Temp. 45° 80 80	Time (hr.) 8 0·75 0·75	$\overbrace{\substack{(\rm XXVII) + \\ (\rm XXVIII) \\ 14 \\ 13 \\ 20 \\ 45 \\ \end{array}}^{\rm (XXVIII)}$	$(I)$ $\overline{40}$ $2$	(III) 46 15 36 	(IV) 1.8 5.8 1.2 43	(XIX)	

<sup>*a*</sup> In the presence of *p*-benzoquinone (50 mg.). <sup>*b*</sup> Under the conditions of the 'wet' Prévost reaction; ratio of (XXVII): (XXVIII) = 2.5:1.

Mechanism of Oxidation of trans- $\beta$ -Methylstyrene by Lead Tetra-acetate.—The rate constant for the secondorder, heterolytic reaction of lead tetra-acetate with trans- $\beta$ -methylstyrene is 70 times smaller than that <sup>2</sup> for reaction with styrene. From a consideration of electronic factors we should have expected that the methylstyrene would be the more reactive; for example, transbut-2-ene reacts about 30 times faster than propylene with bromine in methanol.<sup>18</sup> We infer that the initial addition to give the adduct [XXIX; X = Pb(OAc)<sub>3</sub>] is strongly retarded by steric factors; an indication of such steric hindrance has also been noted in the reactions of the compounds Ph<sub>3</sub>C·CH=CH<sub>2</sub> and Ph<sub>3</sub>C·CM==CH<sub>2</sub> with lead tetra-acetate, the former being the more reactive.<sup>13</sup>

The formation of the adduct (XVI) shows the same <sup>18</sup> J. E. Dubois and G. Barbier, *Tetrahedron Letters*, 1965, 1217.

characteristics as that of the analogue from styrene; that is, it is facilitated by the presence of a catalytic quantity of Perkadox (cf. expts. 7 and 9) and is retarded by the presence of an inhibitor for free-radical reactions (cf. expts. 8 and 10). When allowance is made for the fact that the heterolytic reaction is much slower for trans- $\beta$ methylstyrene than for styrene, it is apparent from comparison of the yields of the adducts (XVI) and (I), respectively, that the homolytic reaction is also slower for *trans*- $\beta$ -methylstyrene. Further, the reduction in the yield of (XVI) on the addition of p-benzoquinone is not nearly so great as in the corresponding reaction of styrene, indicating that the propagating chains are shorter with the former olefin. This might be because of steric hindrance to the uptake of a methyl radical at the  $\beta$ -carbon atom and/or steric hindrance to the oneelectron oxidation of the resulting radical, PhCH·CHMe<sub>2</sub>. Steric hindrance for the former reaction is to be expected from data for the methyl affinities for these olefins in 2,2,4-trimethylpentane solution at  $65^{\circ}$ ; that for styrene is more than eight times as great as that for trans- $\beta$ methylstyrene.19

The diastereoisomeric 1,2-diacetates (XVII) and (XVIII) could also result from a homolytic reaction, as we have shown for styrene and  $\alpha$ -methylstyrene. Confirmatory evidence for this route is difficult to obtain because the reaction times were long enough for there to be a significant degree of acetylation of the hydroxyacetates. However, the yields of the 1,2-diacetates were increased when Perkadox was present, in accord with their formation, at least in part, by the homolytic mechanism. The yields of the 1,2-diacetates were barely affected by the addition of an inhibitor (cf. expts. 8 and 10), possibly because the increased reaction time allowed a greater extent of conversion of the hydroxyacetates into the diacetates.

Comparison of experiments 12 and 13 with 7 and 8, respectively, shows that the yields of the hydroxyacetates (XX) and (XXI) are appreciably reduced when oxygen is excluded; independent experiments (see below) established that a significant fraction of the hydroxyacetates in experiments 7 and 8 can arise *via* autoxidation. However, the addition of one equivalent of water to the reaction at 80° under nitrogen increased the yield of hydroxyacetates from a trace (<0.5%) to 10%, so that in these conditions the hydroxyacetates are formed essentially completely by lead tetra-acetate oxidation.

By acetylating the crude reaction mixture, determining the yields of the diastereoisomeric 1,2-diacetates (XVII) and (XVIII), and subtracting the yields of these compounds present before acetylation (since these may result partly from a homolytic reaction), it was possible to calculate the ratio of *threo*- to *erythro*-isomers in the hydroxyacetates (Table 2). As expected, the most extreme ratio was obtained under the conditions of experiment 14, for there is no reason why the autoxidation responsible for production of the hydroxyacetates in

<sup>19</sup> F. Carrock and M. Szwarc, J. Amer. Chem. Soc., 1959, 81, 4138.

experiments 7—10 should be stereospecific. Thus, the degree of stereospecificity of the 'wet' lead tetraacetate oxidation of *trans*- $\beta$ -methylstyrene (*threo* : *erythro* = 85 : 15) is almost as great as that of the 'wet' Prévost reaction (91 : 9).

These values indicate the predominance of an overall cis addition to the olefin. For the Prévost reaction, the mechanism  $^{20,21}$  is shown in Scheme 2 (X = I); the observed high degree of stereospecificity requires that the iodine atom in the carbonium ion (XXIX) interacts sufficiently strongly with the positively charged carbon atom to prevent the occurrence of rotation about the new C-C single bond for all but a small proportion of the reacting molecules. To the extent that this carbonium ion is stabilised by delocalisation of the charge over the aromatic ring, iodine-participation as represented in the structure (XXIX) should be less significant than in an analogous ion from an aliphatic olefin such as cyclohexene. (The lower degree of stereospecificity in the 'wet' Prévost reaction on 1,2-dimethylcyclohexene than on cyclohexene has been attributed to the facts that the methyl substituents should help to stabilise the initial carbonium ion, thereby reducing iodine-participation, and that these substituents eclipse each other in the fully formed iodonium ion.22)

We have shown previously that the (heterolytic) oxidation of olefins by lead tetra-acetate and by the Prévost procedure are essentially similar in character and, in particular, that both oxidants yield a carbonium ion, or incipient carbonium ion, at each of two phases of the reaction.<sup>13</sup> The present results are in accord with this view [Scheme 2;  $X = Pb(OAc)_3$ ], and indicate the



further similarity that the electrophilic lead species is able to prevent rotation about the new single bond in the carbonium ion [XXIX;  $X = Pb(OAc)_{3}$ ], although not quite so effectively as iodine in the ion (XXIX; X = I).

Of particular note is the absence of products of phenyl-migration in the oxidation of trans-\beta-methylstyrene under all conditions; thus, 2-phenylpropionaldehyde or its 1,1-diacetate, which would have been detected if present in greater than 0.2% yield, was never observed. This is in contrast to the behaviour of both styrene<sup>2</sup> and  $\alpha$ -methylstyrene, where rearrangement products are dominant amongst the products of the heterolytic oxidation paths. Now, both the products of phenyl-migration and a proportion of the hydroxyacetates (depending on the conditions; see above) are formed from a common intermediate for each olefin, namely, the adduct (XXXIII). For both styrene and  $\alpha$ -methylstyrene, phenyl-migration is preferred to acetoxy-participation when the C-Pb bond of this adduct undergoes heterolysis, whereas for trans-βmethylstyrene the converse is the case. A possible explanation is as follows. The carbonium ion formed by heterolysis of the C-Pb bond in (XXXIIIc) should be more stable than those formed from (XXXIIIa, b) since the first is a secondary carbonium ion. Consequently, less assistance should be necessary from the  $\beta$ -phenyl or the  $\beta$ -acetoxy-group in order for the transition state to be reached in the heterolysis of (XXXIIIc) than of (XXXIIIa, b). Now, the effectiveness of a phenyl substituent in stabilising an electron-deficient transition state is especially sensitive to the need for the supply of an electron-pair at that transition state; for example, the reactivity at the *para* position is greater for toluene than biphenyl towards most electrophilic reagents, but as the electrophilic species becomes decreasingly reactive so that the call on the release of an electron-pair at the transition state increases, the reactivity at the para position in biphenyl approaches that in toluene and finally, for uncatalysed bromination, becomes greater; this can be described as reflecting the greater polarisability of a p-phenyl than a p-methyl substituent.<sup>23</sup> This example refers to a case in which the phenyl group is directly conjugated to the electron-deficient transition state, but there is no reason why it should not apply to cases in which the interaction is via a bridged system, and if so, then provided that the polarisability of a  $\beta$ -phenyl substituent is greater than that of a  $\beta$ -acetoxysubstituent, the present results can be accounted for.

In the Prévost reactions also,  $\alpha$ -methylstyrene gave a product characteristic of phenyl-migration whereas *trans*- $\beta$ -methylstyrene did not. However, the yield of this product (5.6%) was far lower than that of the 1,2diacetate which arises *via* the acetoxonium ion. According to our suggestion above, this may be because cleavage of the C-I bond in the intermediate (XXXIV; R = Me, X = I) has made less progress at the transition state than cleavage of the C-Pb bond in [XXXIV; R = Me, X = Pb(OAc)<sub>3</sub>]; a smaller fraction of a positive charge would be present at the transition state for reaction of the iodide than for the Pb<sup>IV</sup> compound, so that there

<sup>&</sup>lt;sup>20</sup> R. B. Woodward and F. V. Brutcher, J. Amer. Chem. Soc., 1958, **80**, 209.

 $<sup>^{21}</sup>$  F. D. Gunstone, in 'Advances in Organic Chemistry, Methods and Results,' ed. R. A. Raphael *et al.*, Interscience, New York, vol. 1, 1960, p. 103.

<sup>&</sup>lt;sup>22</sup> C. A. Bunton and M. D. Carr, J. Chem. Soc., 1963, 770.

<sup>&</sup>lt;sup>23</sup> J. R. Knowles, R. O. C. Norman, and G. K. Radda, J. Chem. Soc., 1960, 4885.

would be less demand for phenyl-participation in the former case.



The different characteristics of 3-phenyl- as compared with  $\beta$ -acetoxy-participation can also underlie another feature of our results, namely that, for corresponding conditions, the extent of phenyl-migration as compared with the other heterolytic reactions is greater for  $\alpha$ methylstyrene than for styrene, with both lead tetraacetate and in the 'wet' Prévost reaction. When the C-X bond of the intermediate [XXXIV; R = H or Me,  $X = Pb(OAc)_{2}$  or I] undergoes heterolysis, the accompanying phenyl-participation leads to a carbonium ion which can be represented as a hybrid of the structures (XXXV--XXXVII; R = H or Me), and acetoxyparticipation leads to the cyclic acetoxonium ion (XXXVIII; R = H or Me). In the corresponding transition states in which these ions have been partly formed, the  $\alpha$ -carbon atom should bear a partial positive charge for phenyl-migration [cf. structure (XXXVII)] but not for acetoxy-participation, so that the electronreleasing methyl group at the  $\alpha$ -carbon atom in [XXXIV; R = Me, X = I or  $Pb(OAc)_3$  should facilitate phenylmigration relative to acetoxy-participation, as compared with the situation for [XXXIV; R = H, X = I or  $Pb(OAc)_3$ ]. The significance of such stabilisation at the migration origin for other reactions brought about by lead tetra-acetate which involve phenyl-migration has been noted before.<sup>24</sup>

The characteristics of the oxidation of  $cis-\beta$ -methylstyrene by lead tetra-acetate (Table 3) closely resemble those for the *trans*-compound except that, as a result of the stereospecificity of the reactions leading to the hydroxyacetates, the erythro-isomer predominates. Under the conditions of experiment 19, in which the hydroxyacetates are produced by reaction of water with the acetoxonium ion and not by autoxidation (cf. experiment 18), the threo-: erythro-ratio is 31:69; in the 'wet' Prévost oxidation, the corresponding ratio is 18:82. The degree of stereospecificity of each reaction is less than in the corresponding oxidation of the *trans* isomer. This is understandable because, to the extent

<sup>24</sup> R. O. C. Norman and R. A. Watson, J. Chem. Soc. (B), 1968, 184, 692.

that a proportion of the species [XXIX; X = I or Pb(OAc)<sub>3</sub>] and the corresponding species from the cisolefin can undergo rotation about the new C-C single bond, equilibrium between the two should favour the former (in which the phenyl and methyl substituents are trans to each other), so that there should be a preponderance of the *threo*-hydroxyacetate.

Autoxidations.—We observed previously that a small quantity of benzaldehyde is formed during the oxidation of styrene with lead tetra-acetate,<sup>2</sup> and in the present work  $\alpha$ -methylstyrene and the two  $\beta$ -methylstyrenes gave acetophenone and benzaldehyde, respectively, during both lead tetra-acetate and Prévost oxidations. For the lead tetra-acetate reaction, the yield of carbonyl compound is inversely related to the reactivity of the olefin towards the oxidant (under typical conditions, the yields were 7—10% for *trans*- $\beta$ -methylstyrene, 2—3% for styrene, and 0.4% for  $\alpha$ -methylstyrene), suggesting that the carbonyl compound accumulates with time independently of the main oxidation. Moreover, the yield of benzaldehyde from each of the  $\beta$ -methylstyrenes was reduced considerably when reaction was carried out under nitrogen, implying that it is formed by autoxidation.

Styrene can be oxidised by oxygen to a significant extent at 50—70° to give benzaldehyde, formaldehyde, styrene oxide, and a polyperoxide of uncertain structure; 25 likewise, a-methylstyrene gives acetophenone, formaldehyde, 2-phenylpropene oxide, and a polyperoxide.<sup>26</sup> We investigated the autoxidation of these olefins and of trans- $\beta$ -methylstyrene under conditions corresponding to those for the oxidations but in the absence of the oxidant, finding that in each case the appropriate carbonyl compound was formed together with the hydroxyacetates and, from  $\alpha$ -methylstyrene, benzyl methyl ketone (Table 5).

TABLE 5

Products from the autoxidation of three styrenes in acetic acid at 60°

Substituent in	Time	Products (%)					
the styrene	(hr.)	Carbonyl compound	Hydroxy-acetates				
None	4	0.1 °	Trace d				
α-Me <sup>a</sup>	0.5	0.01 °	Trace <sup>d</sup>				
trans-β-Me	16	1.0	0.5				
trans-β-Me <sup>b</sup>	16	15	14				
a Benzyl m	ethyl	ketone $(0.03\%)$ was a	lso observed. 👌 In				
the presence	of anh	ydrous lead diacetate	(0.01  mole);  small				

quantities of the diacetates (ca. 1% of each) were also present. • Reproducible to within a factor of 2. d < 0.04%.

Two features of these results are notable. First, simple aerial oxidation cannot account for all the carbonyl compound formed during the lead tetra-acetate oxidations; and secondly, lead diacetate has a marked effect on the yields of products from trans- $\beta$ -methylstyrene. The catalysis of autoxidation by transition-

<sup>25</sup> F. Dukta and D. Gal, Internat. J. Appl. Radiation Isotopes,

 <sup>1962, 13, 27.
 &</sup>lt;sup>26</sup> F. R. Mayo and A. A. Miller, J. Amer. Chem. Soc., 1958, 80, 2480.

metal compounds is well established,<sup>27</sup> but we are not aware of previous reports that lead(II) salts act in this way; the possibility that a transition-metal ion impurity in the lead diacetate is the effective catalyst cannot be ruled out, although the sample of lead diacetate was claimed to contain less than 0.002% iron or copper. However, even the effect of lead diacetate cannot account for the entire yield of benzaldehyde under the conditions of experiment 7, where most of the olefin is being diverted along other reaction paths and lead(II) is only accumulating slowly, and it is possible that lead(IV) is the principal catalytic agent.

Both the carbonyl compounds and the hydroxyacetates are presumably formed by a pathway of the type suggested by van Helden et al.<sup>28</sup> for the formation of acetophenone and the hydroxyacetate (VII) in the radical-catalysed autoxidation of  $\alpha$ -methylstyrene. Benzyl methyl ketone could be formed from  $\alpha$ -methylstyrene by rearrangement of the (expected <sup>26</sup>) intermediate epoxide; a compound whose retention time was in the range expected for this epoxide was present after the autoxidation as well as after lead tetra-acetate oxidation.

Table 5 shows that autoxidation can account for a considerable fraction of the hydroxyacetates formed from trans-\beta-methylstyrene during oxidation by lead tetra-acetate. Acetylation of the crude mixture followed by analysis of the stereoisomeric 1,2-diacetates showed that the threo-: erythro-ratio of the hydroxyacetates was 52:48; that is, there is no significant stereospecificity. This is in contrast to the high degree of stereospecificity of the heterolytic reaction under the conditions of experiment 14, where the incursion of autoxidation is negligible.

A further route to the carbonyl compounds is apparently by oxidation of hydroxyacetates by lead tetraacetate. We found that the oxidation of a mixture of the hydroxyacetates (XXVII) and (XXVIII) under the conditions of experiment 21 gave 0.4% benzaldehyde and

PhCH-CH<sub>2</sub>OAc 
$$\xrightarrow{Pb(OAc)_4}$$
 PhCH-CH<sub>2</sub>OAc  $\xrightarrow{-\cdot Pb(OAc)_3}$   
OH OPb(OAc)<sub>3</sub>  
PhCH-CH<sub>2</sub>OAc  $\longrightarrow$  PhCHO +  $\cdot CH_2OAc$ 

5.6% of the 1,2-diacetate, with 85% of unchanged material; after 40 hr., when the lead tetra-acetate had all been consumed, the yields were 5% of benzaldehyde, 58% of the diacetate, and 27% of unchanged material. However, this process, which is likely to involve homolysis of an O-Pb bond as shown in Scheme 3 (cf. refs. 24,

28), cannot account for a significant fraction of the benzaldehyde<sup>2</sup> formed during the oxidation of styrene by lead tetra-acetate.

#### EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were measured for solutions in deuteriochloroform on a Perkin-Elmer R 10 60 Mc./sec. spectrometer. Mass spectra were determined on an AEI MS12 spectrometer which was coupled via a heated capillary to a gas chromatograph. M.p.s were taken on a Kofler microhot-stage apparatus and are uncorrected.

Gas chromatography was on a Pye instrument (Series 104, model 24), with 6 ft. columns containing 20% Carbowax 20M, 10% silicone oil (SE30), or 10% Apiezon-L, each coated on Celite and operated at 195°, 160°, and 160°, respectively. When yields were to be measured, the Carbowax-containing column was employed and p-nitrotoluene was used as a standard. A hydrogen-inject flame ionisation detector gave a linear response, and the relationship between the quantity of a material injected and its peak-area was established by analysis of synthetic mixtures. Yields so determined were reproducible to within  $\pm 3\%$  of the value quoted.

Acetic acid and benzene were analytical reagents. Lead tetra-acetate (B.D.H. laboratory reagent) was recrystallised before use from acetic acid containing 2% of acetic anhydride, washed with acetic acid, and sucked dry at the pump; the resulting slightly moist material could be handled in the atmosphere without its surface becoming brown through hydrolysis. Iodometric titration showed that the solid contained 90% of lead tetra-acetate and allowance was made for 10% of acetic acid when the material was weighed. Before use in benzene, the material was dried for 48 hr. in a desiccator (KOH). a-Methylstyrene and trans- $\beta$ -methylstyrene were commercial materials which were purified by distillation; their purities were checked by gas chromatography.

cis-\beta-Methylstyrene was obtained by the reduction of methylphenylacetylene by a modification of Brown and Zweifel's method.<sup>29</sup> The acetylene (15 g.) was added to a solution of sodium borohydride (3 g.) in diglyme (50 ml.) and the apparatus was flushed with nitrogen. Boron trifluoride-ether complex (15 ml.) was added to the ice-cold solution during 1 hr. and the solution was allowed to warm to room temperature. (When the solution was stirred during this addition, the yield of  $cis-\beta$ -methylstyrene was reduced to only ca. 5%). After a further hr., ethylene glycol was added cautiously to decompose the excess of borohydride, followed by acetic acid (30 ml.). After standing overnight, the solution was poured into water and the ether extract was washed with sodium carbonate solution and with water and was dried (MgSO4). Evaporation of the solvent and distillation of the residue on a spinningband column gave  $cis-\beta$ -methylstyrene (6.5 g.; 43%) as a colourless liquid, b.p. 167-168° (lit., 30 166.7°); n.m.r. spectrum: aromatic singlet (5H) at 7 2.76, doublet of doublets (1H) centred at  $\tau$  3.60 (J 11.5, J' 1.5 c./sec.) ( $\alpha$ -CH), multiplet (1H) centred at  $\tau$  4.26 analysable as a doublet of quartets (J 11.5, J" 7.0 c./sec.) ( $\beta$ -CH), and doublet of doublets (3H) centred at  $\tau$  8.13 (J' 1.5, J'' 7.0

<sup>&</sup>lt;sup>27</sup> W. A. Waters and J. S. Littler, in 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Part A, Academic Press, 1965, ch. 3; W. H. Richardson, *ibid.*, ch. 4.
<sup>28</sup> R. van Helden, A. F. Bickel, and E. C. Kooyman, *Rec. Trav. chim.*, 1961, **80**, 1257.

<sup>29</sup> H. C. Brown and G. Zweifel, J. Amer. Chem. Soc., 1959, 81,

<sup>1512.</sup> <sup>30</sup> K. N. Campbell and M. J. O'Connor, J. Amer. Chem. Soc., 1939, 61, 2897.

c./sec.) (Me). Gas chromatography showed no trace of the trans isomer.

Reference Compounds.—Products from a-methylstyrene. 2-Phenylallyl acetate, prepared by the method of Hatch and Patton,<sup>31</sup> had b.p. 78-81°/0.7 mm. (lit.,<sup>31</sup> 112-113°/5 mm.); n.m.r. spectrum: aromatic singlet (5H) at  $\tau$  2.68, very narrow multiplets at  $\tau 4.50$  and 4.69 (each 1H) (olefinic protons) and at  $\tau$  5.04 (2H) (methylene protons), and singlet (3H) at  $\tau$  8.00 (OAc).

2-Phenylbut-2-yl acetate was prepared by heating 2phenylbut-2-yl alcohol (7.7 g.) with sodium acetate (12 g.) in acetic anhydride (60 ml.) at 125° for 15 hr. The solution was poured, cold, into water, and the ether extract was washed with sodium carbonate solution and with water and was dried (MgSO<sub>4</sub>). The solvent was evaporated, and distillation of the residue gave 2-phenylbut-2-yl acetate (5.1 g.; 52%), b.p. 78-79°/1.9 mm. (cf. ref. 32); n.m.r. spectrum: aromatic singlet (5H) at  $\tau$  2.74, quartet centred at  $\tau$  7.98 (J 7.3 c./sec.) (CH<sub>2</sub>) and singlet at  $\tau$  8.00 (OAc) (total 5H), singlet (3H) at  $\tau 8.22$  [Me on C(2)], and triplet (3H) centred at  $\tau$  9.25 (J 7.3 c./sec.) [Me on C(3)] (Found: C, 75.0; H, 8.4. Calc. for  $C_{12}H_{16}O_2$ : C, 75.0; H, 8.1%).

2-Oxo-1-phenylprop-1-yl acetate was prepared by a modification of Tanaka's method.<sup>33</sup> Benzyl methyl ketone (10 g.) and lead tetra-acetate (45 g.) were heated in acetic acid at  $100^{\circ}$  for 1.5 hr. and the cooled solution was poured into water. The ether extract was washed with sodium carbonate solution and with water, and was dried  $(MgSO_4)$ . Evaporation of the solvent left a red liquid which was distilled to give, successively, unchanged ketone and 2-oxo-1-phenylprop-1-yl acetate (4·4 g.; 33%), b.p. 83-84°/0·4 mm. (lit.,<sup>34</sup> 134°/10 mm.); n.m.r. spectrum: aromatic singlet (5H) at  $\tau 2.62$ , singlet (1H) at  $\tau 4.03$  (CH), and singlets (6H in all) at  $\tau$  7.87 and 7.93 (OAc and Me).

1-Phenylpropen-2-ol acetate was obtained by heating benzyl methyl ketone (6.7 g.) with pyridine (20 ml.) in acetic anhydride (40 ml.) at 140° for 40 hr. The ether solution of the residue which was obtained by concentration under reduced pressure was washed with sodium carbonate solution and with water and was dried (Na<sub>2</sub>CO<sub>3</sub>). Evaporation of the solvent followed by distillation of the residue gave, successively, unchanged ketone and a mixture of the two geometrical isomers of 1-phenylpropen-2-ol acetate (4.6 g.; 52%), b.p. 71--73°/0.4 mm. (lit., 35.67--69°/0.8 mm.); n.m.r. spectrum: aromatic singlet (5H) at  $\tau$  2.76, narrow multiplets (total 1H) at  $\tau$  3.77 and 4.11 (vinylic proton; two isomers), singlets at  $\tau$  7.91 and 8.18 (OAc; two isomers) and narrow multiplet at  $\tau$  7.95 (Me) (6H in all).

2-Phenylpropane-1,2-diol 1-acetate was prepared by the addition of pulverised iodine (5.1 g.) to a stirred solution of  $\alpha$ -methylstyrene (2.4 g.) and silver acetate (8.4 g.) in acetic acid (60 ml.) containing water (0.56 g.). After 1 hr. at room temperature, the solution was heated for 3 hr. at 100° and then cooled. The precipitated silver salts were filtered off and washed with ether. A small portion (ca. 5 ml.) of the combined filtrates was preserved. The remainder was poured into water and the ether extract was washed with sodium carbonate solution and with water and was dried  $(MgSO_{4})$ . Evaporation of the solvent and distillation of the residue gave a fraction, b.p. 82-83°/0.15 mm., which was redistilled to give 2-phenylpropane-1,2-diol 1-acetate

<sup>31</sup> L. F. Hatch and T. L. Patton, J. Amer. Chem. Soc., 1954, 76, 2705.

<sup>32</sup> D. J. Cram, J. Amer. Chem. Soc., 1952, 74, 2137.
 <sup>33</sup> K. Tanaka, Jap. Pat. 178,312 (Chem. Abs., 1951, 45, 8556).

(1.2 g., 30%), b.p. 84°/0.15 mm. (lit., 3 66°/0.01 mm.); n.m.r. spectrum: aromatic multiplet (5H) at  $\tau$  2.4-2.8, singlet (2H) at  $\tau$  5.80 (CH<sub>2</sub>), broad singlet (1H) at  $\tau$  7.25 which was removed by the addition of  $D_2O$  (OH), singlet (3H) at  $\tau$ 8.01 (OAc), and singlet (3H) at  $\tau$  8.47 (Me) (Found: C, 68.3; H, 7.2. Calc. for  $C_{11}H_{14}O_3$ : C, 68.0; H, 7.3%).

The portion which had been preserved was concentrated under reduced pressure to ca. 1 ml. and acetic anhydride (1 ml.) and concentrated sulphuric acid (1 drop) were added. After standing overnight, the solution was poured into water and the ether extract was washed with sodium carbonate solution and water and was dried  $(MgSO_4)$ . After evaporation of the solvent, the material was analysed by gas chromatography.

2-Phenylpropane-1,2-diol diacetate. a-Methylstyrene (8.9 g.) was added slowly to a cooled and well stirred mixture of formic acid (45 ml.) and 100-volume hydrogen peroxide (10.5 ml.). The solution was kept at  $40^{\circ}$  for 2 hr. and, after standing overnight, was concentrated under reduced pressure to about 10 ml. A solution of sodium hydroxide (10 g.) in water (20 ml.) was added in portions and the mixture was heated at 45° for 2 hr. The chloroform extract of the cooled solution was dried  $(Na_2CO_3)$ , the solvent was evaporated, and the brown oily residue was distilled to give acetophenone and then 2-phenylpropane-1,2-diol (6.0 g., 52%) as a colourless liquid, b.p. 86%/0.3 mm., which solidified on standing and had m.p.  $40-43^{\circ}$  (lit., <sup>36</sup>  $44^{\circ}$ ); n.m.r. spectrum: aromatic singlet (5H) at  $\tau$  2.68, broad singlets (4H in all) at  $\tau$  6.40, 6.70, and 7.05 (CH<sub>2</sub> and OH) which, on addition of D<sub>2</sub>O, became a sharp AB system centred at  $\tau$  6.44, and a singlet (3H) at  $\tau$  8.54 (Me). This diol (5.5 g.) was heated with sodium acetate (8 g.) in acetic anhydride (20 ml.) at  $125^{\circ}$  for 5 hr. and the excess of the anhydride was decomposed by the cautious addition of water. The solution was poured into water, and the ether extract was washed with sodium carbonate solution and with water and was dried  $(MgSO_4)$ . Evaporation of the solvent and distillation of the residue gave a small quantity of 2-phenylallyl acetate (identified by comparison with an authentic sample) and then 2-phenylpropane-1,2-diol diacetate (6.8 g., 80%) as a colourless, viscous liquid, b.p.  $97^{\circ}/0.35$  mm.; n.m.r. spectrum: aromatic singlet (5H) at  $\tau$  2.69, singlet (2H) at  $\tau$  5.64 (CH<sub>2</sub>), two singlets (6H in all) at  $\tau$  7.95 and 7.99 (OAc), and singlet (3H) at  $\tau$  8.11 (Me) (Found: C, 66.4; H, 6.7. C<sub>13</sub>H<sub>16</sub>O<sub>4</sub> requires C, 66.1; H, 6.8%).

An attempt was made to prepare benzyl methyl ketone diacetate by the slow addition of the ketone (2.7 g) to an ice-cold solution of acetic anhydride (5 ml.) containing boron trifluoride-ether complex (6 drops). After the mixture had been stirred for 1 hr., 10% sodium acetate solution (15 ml.) was added. After a further 1 hr., the solution was extracted with ether and the extract was washed with sodium carbonate solution and dried ( $MgSO_4$ ). Evaporation of the solvent left a yellow liquid (3 g.) whose n.m.r. spectrum showed that the major component was unchanged ketone. However, there were also resonances at  $\tau$  6.56, 8.01, and 8.18 in the ratio 2:6:3, which can be tentatively assigned to the ketone diacetate. Attempts to isolate this compound by column chromatography and fractional distillation were unsuccessful.

<sup>34</sup> G. F. Hennion and W. S. Murray, J. Amer. Chem. Soc., 1942, 64, 1220.

<sup>35</sup> G. G. Smith, J. Amer. Chem. Soc., 1953, 75, 1134.

<sup>36</sup> I. Heilbron and H. M. Bunbury, 'Dictionary of Organic Compounds,' 4th edn., Eyre and Spottiswoode, London, 1965.

Products from cis- and trans-β-methylstyrene. 2-Methyl-1phenylprop-1-yl acetate was obtained by heating 2-methyl-1-phenylpropan-1-ol<sup>37</sup> (14.4 g.) with sodium acetate (4 g.) in refluxing acetic anhydride for 15 hr. After excess of the anhydride had been decomposed by the cautious addition of water, the cooled solution was poured into water and the ether extract was washed with sodium carbonate solution and with water and was dried (MgSO<sub>4</sub>). Evaporation of the solvent and distillation of the residue yielded the acetate (13.3 g.; 72%), b.p. 70°/1.3 mm. (lit., 37 118-120°/16 mm.); n.m.r. spectrum: aromatic singlet (5H) at  $\tau$  2.67, doublet (1H) centred at  $\tau$  4.52 (J 7.2 c./sec.) [proton on C(1)], singlet at  $\tau$  7.99 and distorted octet centred at  $\tau$  7.98 (J 7.2, J' = J'' = 6.6 c./sec.) (4H in all) [OAc and proton on C(2)], and two doublets centred at  $\tau$  9.05 and 9.22 (I' = J'' = 6.6 c./sec.) (6H in all) (non-equivalent Me groups) (Found: C, 74.9; H, 8.2. Calc. for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>: C, 75.0; H, 8.4%).

erythro-1-Phenylpropane-1,2-diol diacetate. erythro-1-Phenylpropane-1,2-diol (1 g.), prepared by the oxidation of cis-\beta-methylstyrene by permanganate,38 was heated with sodium acetate (4 g.) in acetic anhydride (16 ml.) at 145° for 16 hr. and excess of the anhydride was then decomposed by the cautious addition of water. The solution was poured into water, and the ether extract was washed with sodium carbonate solution and with water and was dried  $(MgSO_4)$ . Evaporation of the solvent and distillation of the residue gave erythro-1-phenylpropane-1,2-diol diacetate (1.3 g.; 83%) as a colourless liquid, b.p. 91-92°/0.25 mm.; n.m.r. spectrum: aromatic singlet (5H) at  $\tau$  2.70, doublet (1H) centred at  $\tau$  4.10 (J 4.2 c./sec.) [proton on C(1)], quartet of doublets (1H) centred at  $\tau$  4.82 (J 4.2, J' 6.2 c./sec.) [proton on C(2)], singlets (each 3H) at  $\tau$  7.90 and 8.03 (OAc), and doublet (3H) centred at  $\tau$  8.84 (J' 6.2 c./sec.) (Me) (Found: C, 65.8; H, 6.8. C13H16O4 requires C, 66.1; H, 6.8%).

threo-1-Phenylpropane-1,2-diol diacetate was prepared from the diol <sup>38</sup> in the same way as the erythro-isomer and had b.p. 92°/0·35 mm.; n.m.r. spectrum: aromatic singlet (5H) at  $\tau$  2·62, doublet (1H) centred at  $\tau$  4·20 (J 6·7 c./sec.) [proton on C(1)], quintet (1H) centred at  $\tau$  4·69 (J = J' =6·7 c./sec.) [proton on C(2)], singlets (6H in all) at  $\tau$  7·94 and 7·97 (OAc), and doublet (3H) centred at  $\tau$  8·90 (J' 6·7 c./sec.) (Me) (Found: C, 65·8; H, 6·6. C<sub>13</sub>H<sub>16</sub>O<sub>4</sub> requires C, 66·1; H, 6·8%).

2-Phenylpropane-1,1-diol diacetate was prepared by a modification of the method of Man et al.<sup>10</sup> 2-Phenylpropionaldehyde (14 g.) was added during 1.5 hr. to ice-cold acetic anhydride (25 ml.) containing boron trifluoride-ether complex (6 drops). The solution was stirred for 1 hr., 10% sodium acetate solution (90 ml.) was added, and stirring was continued for a further 1 hr. The ether extract was washed with sodium carbonate solution and with water and was dried  $(Na_2CO_3)$ . Evaporation of the solvent and distillation of the residue gave 2-phenylpropane-1,1-diol diacetate (18.8 g.; 76%) as a colourless liquid, b.p.  $106^{\circ}/0.5$ mm.; n.m.r. spectrum: aromatic multiplet (5H) centred at  $\tau$  2.67, triplet (1H) centred at  $\tau$  3.06 (J 5 c./sec.) [proton on C(1)], and unresolved multiplet at  $\tau$  7.0—8.0 [protons on C(2) and C(3)] and singlet at  $\tau$  7.93 (OAc) (10H in all) (Found: C, 66.2; H, 6.9. C<sub>13</sub>H<sub>16</sub>O<sub>4</sub> requires C, 66.1; H, 6.8%).

Attempted Preparation of 1-Phenylethane-1,2-diol 2acetate.—Sodium borohydride (3 g.) in slightly alkaline icecold water (30 ml.) was added slowly, with stirring, to an View Article Online

ice-cold solution of phenacyl acetate (from phenacyl bromide with sodium acetate; m.p.<sup>36</sup> 48.5-49°) (11 g.) in methanol (100 ml.). After 5 min., excess of the borohydride was decomposed with dilute sulphuric acid and the solution was poured into saturated brine. The ether extract was dried  $(MgSO_4)$  and the solvent was distilled to leave a yellow liquid which was heated with lead tetraacetate (25 g.) in acetic acid (100 ml.) for 30 min. at  $60^{\circ}$ to destroy any phenylethane-1,2-diol. The solution was poured into saturated brine and the ether extract was washed with concentrated sodium carbonate solution and was dried (MgSO<sub>4</sub>). The yellow liquid obtained by evaporation of the solvent was distilled to give a colourless oil, b.p. 118-119°/0.75 mm., whose n.m.r. spectrum was consistent with its containing both 1-phenylethane-1,2-diol 2-acetate [aromatic singlet at  $\tau$  2.70, doublet of doublets centred at  $\tau$  5.15 (J 4.8, J' 7.2 c./sec.) (CH), doublets centred at  $\tau$  5.85 (J 4.8 c./sec.) and 5.88 (J' 7.2 c./sec.) (non-equivalent  $CH_2$ -protons), broad singlet at  $\tau$  6.70, removed by the addition of  $D_2O$  (OH), and singlet at  $\tau 8.01$ (OAc)] and the isomeric 1-acetate [aromatic singlet at  $\tau$  2.70, triplet centred at  $\tau$  4.22 (J 5.8 c./sec.) (CH), doublet centred at  $\tau$  6.29 (J 5.8 c./sec.) (CH<sub>2</sub>), broad singlet at  $\tau$  6.70, removed by the addition of  $D_2O$  (OH), and singlet at  $\tau$ 7.98 (OAc)] in the ratio 2.5: 1, together with about 2% of the corresponding diacetate.

Oxidations by Lead Tetra-acetate.—The procedure was the same as for the oxidation of styrene<sup>2</sup> except that one-third quantities were used. A typical experiment was as follows.  $\alpha$ -Methylstyrene (1·2 g.) in acetic acid (6·5 ml.) was added to a stirred suspension of lead tetra-acetate (5 g.) in acetic acid (6·5 ml.) at 60°. After 30 min. the solution was poured into water and the ether extract was washed with sodium carbonate solution and with water and was dried (MgSO<sub>4</sub>). Evaporation of the solvent left a pale yellow oil (1·4 g.) which was analysed by n.m.r. spectroscopy and gas chromatography. In experiments 12—15, 18, and 19 the reactants were mixed at room temperature and flushed with nitrogen for 1 hr. before being heated to the reaction temperature.

Prévost Oxidations of cis- and trans-\u00c3-Methylstyrene.---Pulverised iodine (2.5 g.) was added with stirring to a mixture of trans- $\beta$ -methylstyrene (1.5 g.) and silver acetate (5.2 g.) in acetic acid (38 ml.) containing water (0.35 g.). After 1 hr. at room temperature, the solution was heated for 4 hr. at 100°. Precipitated silver salts were filtered off from the cooled solution and washed with ether. A small portion of the combined filtrates (ca. 5 ml.) was set aside and the remainder was poured into water and the ether extract was washed with sodium carbonate solution and with water and was dried  $(MgSO_4)$ . Evaporation of the solvent followed by distillation of the residue gave a colourless liquid, b.p. 109-110°/0.5 mm., whose n.m.r. spectrum was consistent with its being an essentially pure mixture of the erythro- and threo-isomers of the two 1-phenylpropane-1,2diol monoacetates and gas chromatography of which showed the presence of ca. 3% of the corresponding diacetates.

The portion of the filtrates which had been preserved was concentrated under reduced pressure to ca. 1 ml. and acetic anhydride (3 ml.) and concentrated sulphuric acid (1 drop) were added. After standing overnight, the solution was poured into water and the ether extract was washed with sodium carbonate solution and with water and was dried

<sup>38</sup> M. Svoboda and J. Sicher, Coll. Czech. Chem. Comm., 1955, 20, 1452.

<sup>&</sup>lt;sup>37</sup> A. Favorskii, J. prakt. Chem., 1913, 88, 641.

 $(MgSO_4)$ . The residue after evaporation of the solvent was analysed by gas chromatography.

Styrene and cis- $\beta$ -methylstyrene were oxidised in the same way. For the latter, all the crude mixture was acetylated before gas chromatography.

Autoxidations.—The appropriate olefin (0.01 mole) was dissolved in acetic acid (13 ml.) and heated at constant temperature for a given time (Table 4). Work-up was as for the products from lead tetra-acetate oxidations.

Kinetic Measurements.—The procedure was the same as that used for the oxidation of styrene<sup>2</sup> except that, in the case of *trans*- $\beta$ -methylstyrene, measurements were also made with solutions which were 0.032 and 0.048M in the olefin, each being 0.016M with respect to the oxidant.

We thank the S.R.C. for a Studentship (C. B. T.).

[8/401 Received, March 20th, 1968]