

## 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 ( $k_{\text{rel.}} = 19$ ), 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 stereochemistry 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.

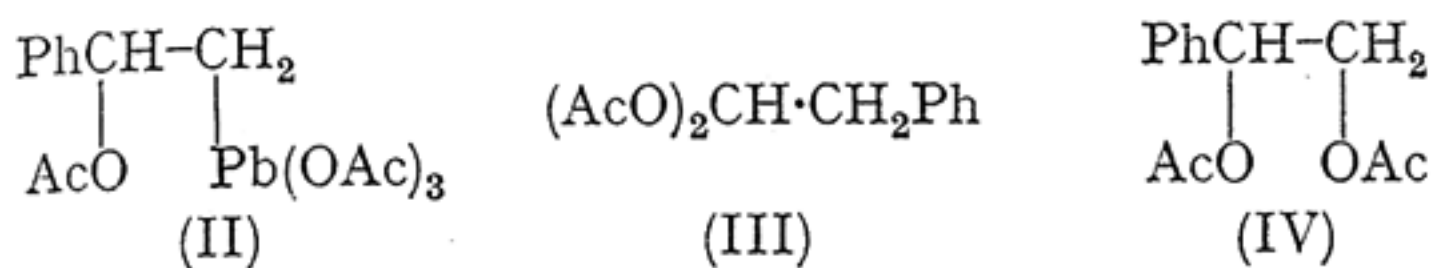
We have previously shown that the oxidation of styrene by lead tetra-acetate occurs simultaneously by homolytic and heterolytic pathways.<sup>2</sup> The former involves a chain reaction in which the propagation steps are thought to be (a) the addition of a methyl radical, probably derived from  $\cdot\text{Pb}(\text{OAc})_3$ , 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

ion, and thence the adduct  $\text{PhCH}(\text{OAc})\text{CH}_2\text{CH}_3$  (I), and the chain-carrying species,  $\cdot\text{Pb}(\text{OAc})_3$ . 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>1</sup> Part XIV, R. O. C. Norman and M. Poustie, *J. Chem. Soc. (B)*, 1968, 781.

<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.<sup>2</sup>



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;<sup>3</sup> 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  $\alpha$ -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 2-acetate (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 ( $M - \text{HOAc}$ ) 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  $(\text{PhCH}=\text{CMeOH})^+$ . [A contribution to this peak might be made by  $(\text{PhCH}_2\cdot\text{COMe})^+$  (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 ( $\text{PhCH}_2\text{CO}^+$ ) 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<sub>2</sub> 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

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

<sup>4</sup> H. R. Hensel, *Chem. Ber.*, 1955, **88**, 527.

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

<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.

<sup>8</sup> R. Criegee, P. Dimroth, K. Noll, R. Simon, and C. Weis, *Chem. Ber.*, 1957, **90**, 1070.

<sup>9</sup> H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, Inc., San Francisco, 1967, p. 168.

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

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 *erythro*-isomers in the

TABLE 1

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

Expt.	Temp.	Time (hr.)	Products (%)								
			(V)	(VI)	(VII)	(VIII)	(IX)	(X) <sup>a</sup>	(XI)	(XII)	(XIII)
1	45°	1.5	0.9	41	15	4.4	4.8	27	—	—	0.4
2	60	0.5	3.2	40	18	4.1	4.7	20	—	—	0.4
3	80	0.25	7.1	40	14	4.7	4.5	17	2.8	1.1	0.4
4	60	18	1.1	46	12	4.7	4.2	0.8	—	5.1	1.8
5 <sup>b</sup>	60	0.5	0.8	25	19	2.6	3.1	15	12	6.6	1.4
6 <sup>c</sup>	80	4	26	12	3.6	11	4.8	21	5.3	—	1.2

<sup>a</sup> 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.). <sup>c</sup> In benzene under reflux.

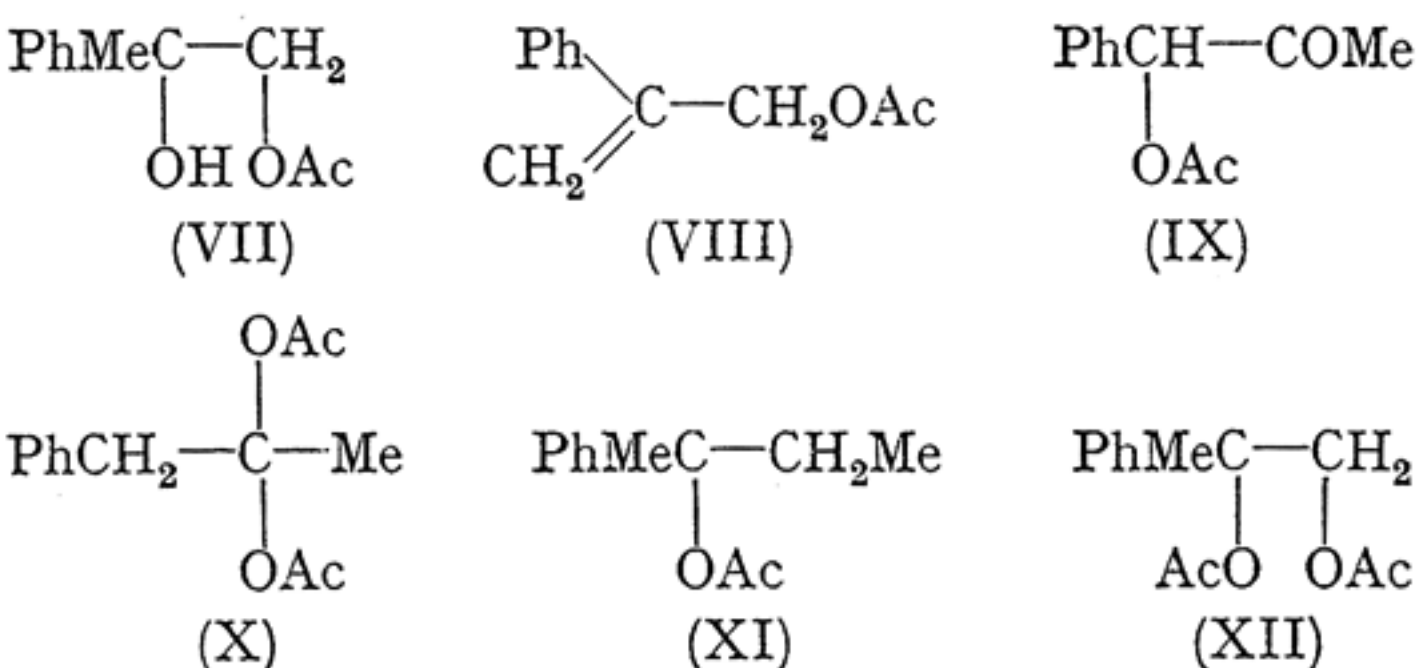
TABLE 2

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

Expt.	Temp.	Time (hr.)	Products (%)							Ratio <sup>a</sup> (XVII) : (XVIII)
			(XIV)	(XVI)	(XVII)	(XVIII)	(XIX)	(XX) + (XXI)		
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 <sup>b</sup>	60	3	1.6	10	23	18	5	25	62 : 38	
10 <sup>c</sup>	80	6	14	3.4	23	9	9	17	65 : 35	
11 <sup>d</sup>	80	48	22	13	20	12	1.9	Trace	—	
12 <sup>e</sup>	60	48	24	4.1	23	8	2.5	1.6	—	
13 <sup>e</sup>	80	10	29	6	19	7	1.3	Trace	—	
14 <sup>e,f</sup>	80	10	15	7	21	9	1.2	10	85 : 15	
15 <sup>e,g</sup>	80	5	15	16	18	10	1.7	1.3	—	

<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> 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>g</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%).



Products from the Oxidation of *cis*- and *trans*- $\beta$ -Methylstyrene.—Oxidation of each olefin by lead tetra-acetate

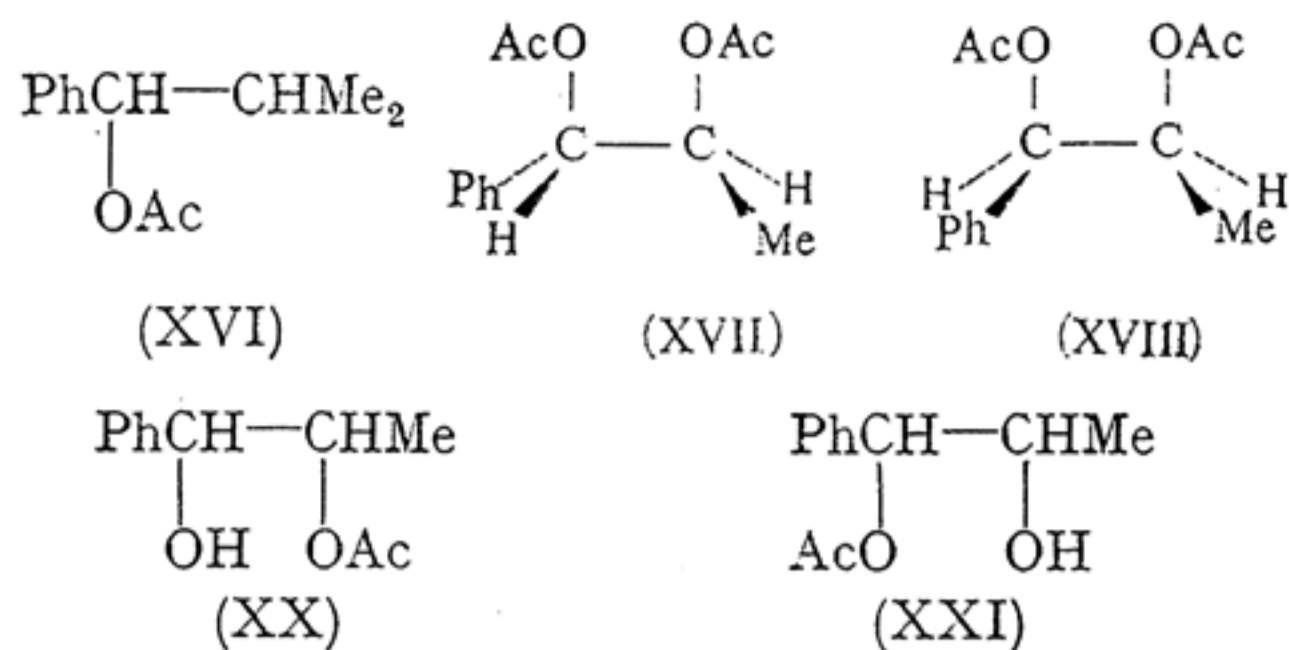
hydroxyacetates were then determined from the gas chromatograms obtained before and after acetylation of the crude product. Two unidentified materials (*ca.* 5%) were formed under most conditions: one was formed from both *cis*- and *trans*- $\beta$ -methylstyrene (as judged by its retention time on 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. Saegbarth, *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  $\alpha$ -methylstyrene than on styrene; thus, at 60° in acetic acid, the second-order 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

Expt.	Temp.	Time (hr.)	Products (%)						Ratio <sup>a</sup> (XVII) : (XVIII)
			(XV)	(XVI)	(XVII)	(XVIII)	(XIX)	(XX) + (XXI)	
16	60°	21	12	0.7	13	10	17	16	38 : 62
17 <sup>b</sup>	60	4	21	8	15	13	8	9	45 : 55
18 <sup>c</sup>	80	13	17	9	33	15	0.4	—	—
19 <sup>c,d</sup>	80	14	12	10	27	16	0.9	10	31 : 69

<sup>a</sup> From acetylation of the hydroxyacetates (XX) + (XXI).

<sup>c</sup> Under nitrogen. <sup>d</sup> In the presence of 1 mol. of water.

<sup>b</sup> In the presence of di-isopropyl peroxydicarbonate (50 mg.).

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 second-order 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 acetoxy-group to the double bond of  $\alpha$ -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° 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-

oxidative rearrangement of *p*-methoxystyrene and some related compounds;<sup>12</sup> 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 tetra-acetate 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 tetra-acetate 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° in acetic acid for 2 hr., it was recovered in 93% yield

<sup>12</sup> R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B)*, 1967, 604.

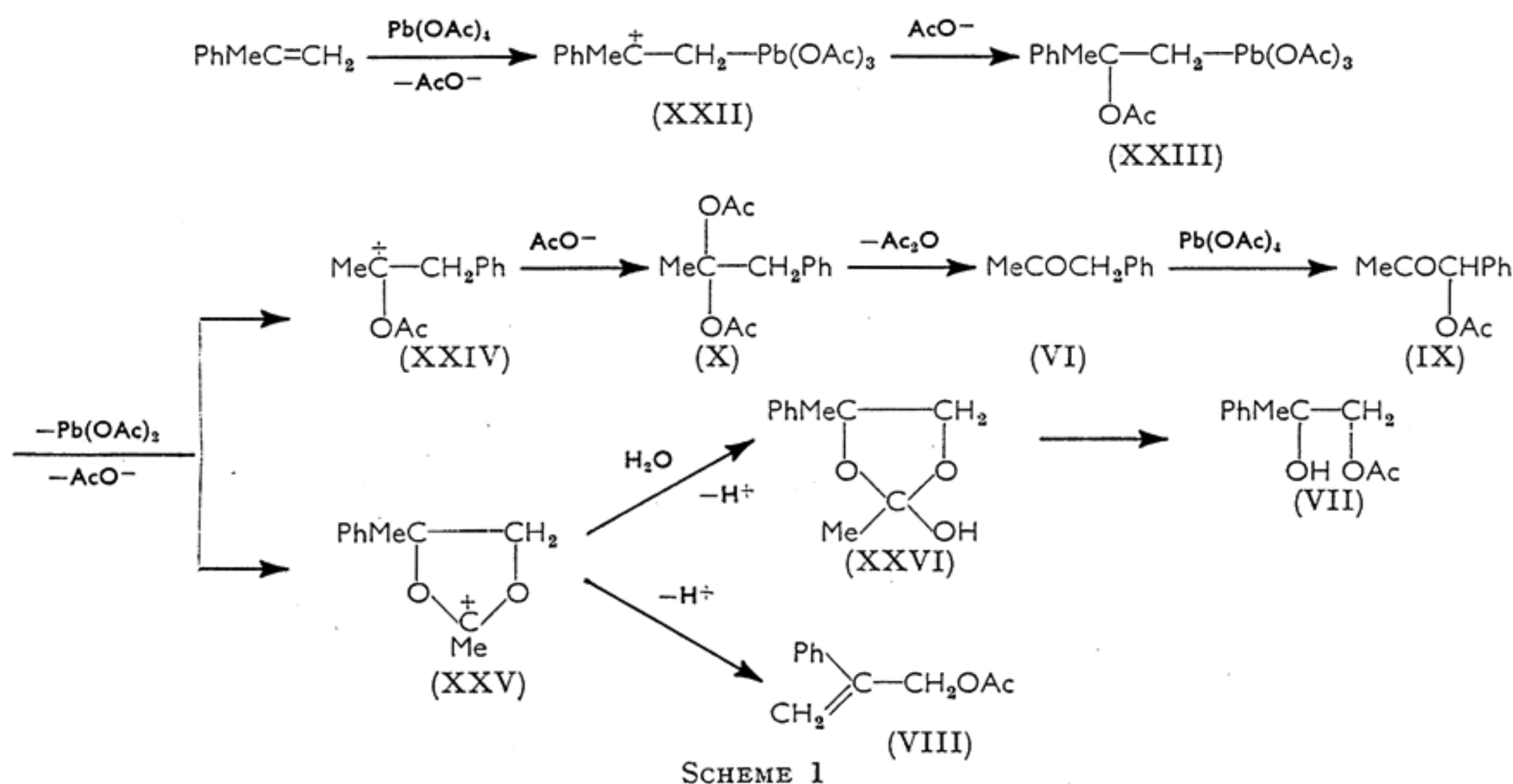
<sup>14</sup> J. D. Bacha and J. K. Kochi, *Tetrahedron*, 1968, **24**, 2215.

<sup>13</sup> R. Criegee, in 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Part A, Academic Press, 1965, ch. 5.

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° 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 1) or from the carbonium ion (XXII) by the sequence (XXII)  $\rightarrow$   $\text{CH}_2=\text{CPh}-\text{CH}_2-\text{Pb}(\text{OAc})_3 \rightarrow \text{CH}_2=\text{CPh}-\text{CH}_2\text{OAc} + \text{Pb}(\text{OAc})_2$ . 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° in acetic acid, *ca.* 7% of the 1,2-diacetate 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

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 4½ 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,  $\text{PhMeC}(\text{OAc})\cdot\text{CH}_2\text{OH}$ , so that our failure to detect the latter compound on oxidation of  $\alpha$ -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.

<sup>15</sup> L. W. Reeves and W. G. Schneider, *Trans. Faraday Soc.*, 1958, **54**, 314.

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 1,2-diacetate (IV) is evidently formed under these conditions by a heterolytic pathway. Secondly, under conditions which favour the homolytic reaction (80°), 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).

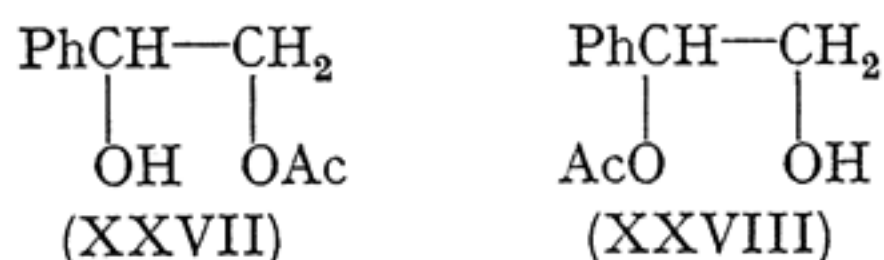


TABLE 4

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

Expt.	Temp.	Time (hr.)	Products (%)				
			(XXVII) + (XXVIII)	(I)	(III)	(IV)	(XIX)
20	45°	8	14	—	46	1.8	4.1
21	80	0.75	13	40	15	5.8	1.0
22 <sup>a</sup>	80	0.75	20	2	36	1.2	1.1
23 <sup>b</sup>			45	—	—	43	2.0

<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-β-Methylstyrene by Lead Tetra-acetate.*—The rate constant for the second-order, heterolytic reaction of lead tetra-acetate with *trans*-β-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, *trans*-but-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·CMe=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

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*-β-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*-β-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 β-carbon atom and/or steric hindrance to the one-electron oxidation of the resulting radical, PhĊH·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°; that for styrene is more than eight times as great as that for *trans*-β-methylstyrene.<sup>19</sup>

The diastereoisomeric 1,2-diacetates (XVII) and (XVIII) could also result from a homolytic reaction, as we have shown for styrene and α-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

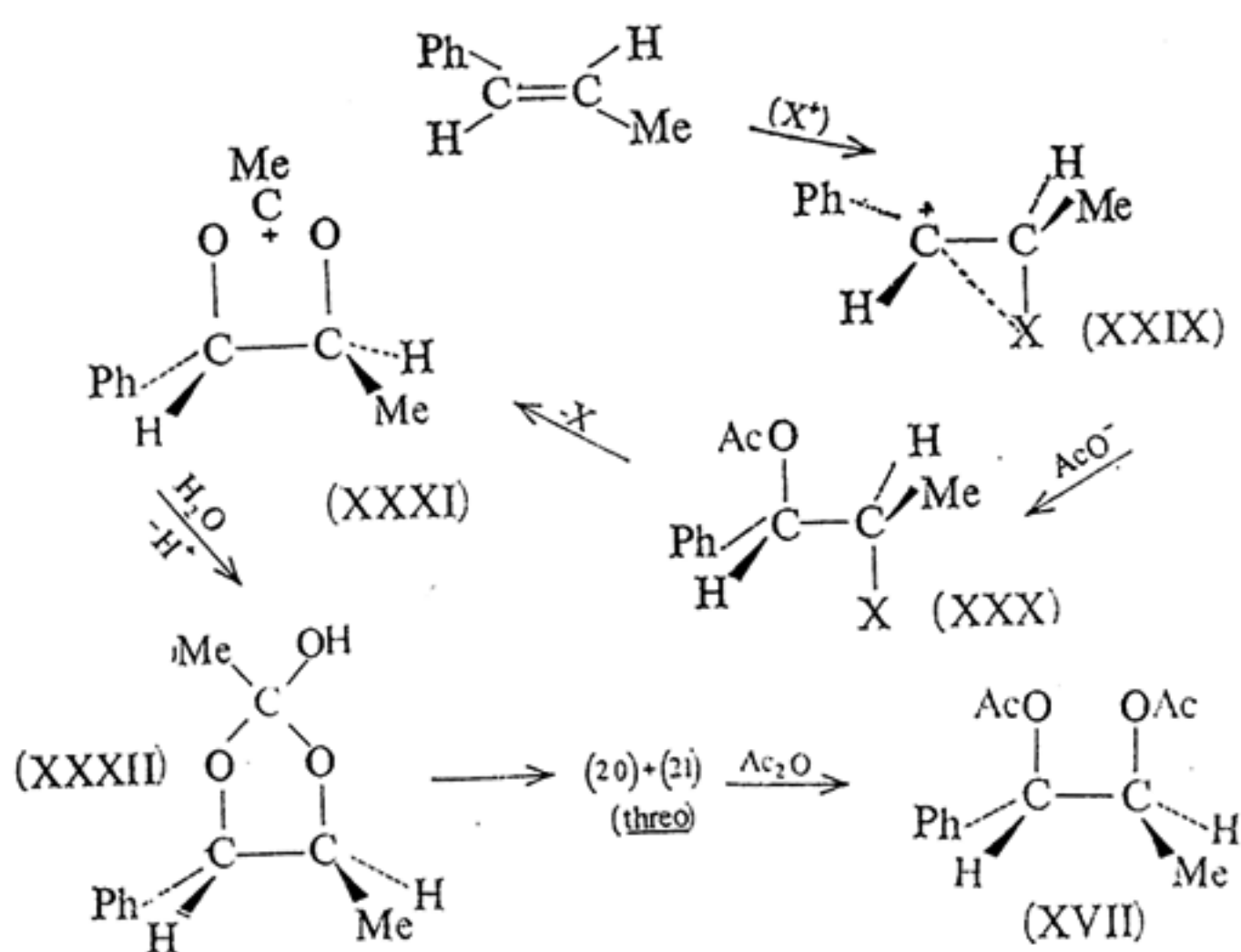
<sup>18</sup> J. E. Dubois and G. Barbier, *Tetrahedron Letters*, 1965, 1217.

<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<sup>20,21</sup> 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.<sup>22</sup>)

We have shown previously that the (heterolytic) oxidation of olefins by lead tetraacetate 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)<sub>3</sub>], and indicate the



SCHEME 2

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)<sub>3</sub>], although not quite so effectively as iodine in the ion (XXIX; X = I).

<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.

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*- $\beta$ -methylstyrene 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  $\beta$ -acetoxy-substituent, 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 1,2-diacetate 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>22</sup> C. A. Bunton and M. D. Carr, *J. Chem. Soc.*, 1963, 770.

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







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

*Reference Compounds.—Products from  $\alpha$ -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 2-phenylbut-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<sub>12</sub>H<sub>16</sub>O<sub>2</sub>: 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° 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<sub>4</sub>). 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.,<sup>35</sup> 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<sub>4</sub>). 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

(1.2 g., 30%), b.p. 84°/0.15 mm. (lit.,<sup>3</sup> 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<sub>2</sub>O (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<sub>11</sub>H<sub>14</sub>O<sub>3</sub>: 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<sub>4</sub>). After evaporation of the solvent, the material was analysed by gas chromatography.

*2-Phenylpropane-1,2-diol diacetate.*  $\alpha$ -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° 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<sub>2</sub>CO<sub>3</sub>), 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° (lit.,<sup>36</sup> 44°); 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° 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<sub>4</sub>). 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°/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<sub>4</sub>). 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.

<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).

*Products from cis- and trans-β-methylstyrene.* 2-Methyl-1-phenylprop-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.,<sup>37</sup> 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 ( $J' = J'' = 6.6$  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-β-methylstyrene* by permanganate,<sup>38</sup> 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<sub>4</sub>). 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. C<sub>13</sub>H<sub>16</sub>O<sub>4</sub> 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<sub>2</sub>CO<sub>3</sub>). 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°/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 2-acetate.*—Sodium borohydride (3 g.) in slightly alkaline ice-cold water (30 ml.) was added slowly, with stirring, to an

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<sub>4</sub>) 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° 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<sub>2</sub>-protons), broad singlet at  $\tau$  6.70, removed by the addition of D<sub>2</sub>O (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<sub>2</sub>O (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-β-Methylstyrene.*—Pulverised iodine (2.5 g.) was added with stirring to a mixture of *trans-β-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<sub>4</sub>). 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-1,2-diol 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>37</sup> A. Favorskii, *J. prakt. Chem.*, 1913, **88**, 641.

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

( $\text{MgSO}_4$ ). 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.

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