Oxidation by Cobalt(III) Acetate. Part 12. Stereoselective Formation of *threo*-1-Phenylpropane-1,2-diol Monoacetate in Oxidation of β-Methylstyrenes Unsubstituted and Substituted with Electron-donating Groups by Cobalt(III) and Manganese(III) Acetate in Acetic Acid

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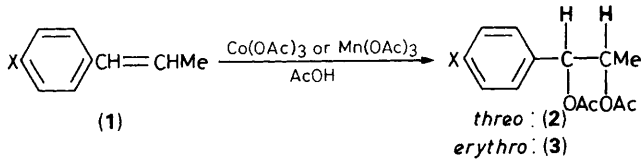
Stereochemistry in oxidation of β-methylstyrenes unsubstituted and substituted with electron-donating groups (H, *p*-MeO, and *p*-Me) by cobalt(III) and manganese(III) acetate in acetic acid or in acetic acid containing trifluoroacetic acid has been studied. *threo*-1-Arylpropane-1,2-diol monoacetates were the main products in the oxidations of both *E*- and *Z*-alkenes by these oxidants. These results are explained in terms of the difference in stabilities between intermediate (**11**) and (**14**).

There are many reports on the oxidation of alkenes by various metallic acetates such as lead(IV),[1-4] thallium(III),[3-5] mercury(II),[3,4,6,7] silver(I) combined with iodine,[8-10] manganese(III),[11] cerium(IV),[12] and cobalt(III) salts. These salts with the exception of cerium(IV) acetate, can react with the double bond in alkenes to give 1,2-diol derivatives. The reaction mechanisms are divided into two classes; (*a*) a reaction *via* metal–carbon bond (or sigma complex) followed by solvolysis [lead(IV), thallium(III), mercury(II), and silver(I)–I_2], (*b*) a reaction involving a one-electron transfer giving radical cation.

In the former mechanism, it is well known that an *E*-alkene gives *threo*-derivatives and a *Z*-alkene gives the *erythro*-isomer, Scheme 1.

On the other hand, little is known of the stereochemistry in the oxidation of alkenes by cobalt(III) acetate, although the stereochemical evidence should give a potent suggestion for the reaction mechanism. This may be due to the fact that there are few examples of the reaction giving 1,2-diol derivatives in the cobalt(III) acetate oxidation of alkenes. For example, aliphatic alkenes undergo allylic oxidation on treatment with cobalt(III) acetate.[13-16] However, we found in our previous paper[17] that cobalt(III) acetate oxidation of electron-rich alkenes gave predominantly 1,2-diol derivatives. Hence, this research was undertaken to clarify the stereochemistry of oxidation of β-methylstyrenes substituted with electron-donating groups (*p*-MeO and *p*-Me) by cobalt(III) acetate. In the course of this research, we found that manganese(III) acetate can also oxidise electron-rich alkenes to give 1,2-diol derivatives and that β-methylstyrene, on oxidation by both oxidants in acetic acid containing trifluoroacetic acid as promoter, gives fairly good yields of the 1,2-diol derivatives. Therefore, the stereochemistry of manganese(III) acetate oxidation of the alkenes to 1,2-diol derivatives is also examined here.

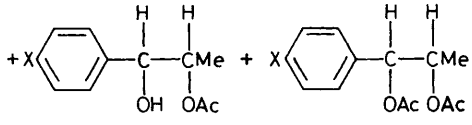


(1) *threo* : (2) *erythro* : (3)

Scheme 1.

a; X = OMe, *E*
b; X = OMe, *Z*
c; X = Me, *E*
d; X = Me, *Z*
e; X = H, *E*
f; X = H, *Z*

(**2–5a**):X = OMe
(**2–5c**):X = Me
(**2–5e**):X = H



threo : (**4**) *erythro* : (**5**) *threo* : (**4′**) *erythro* : (**5′**)

Scheme 2.

Results and Discussion

Oxidation of Anethole.—(*Z*)-Anethole (**1a**) [1-(*p*-methoxyphenyl)propene] was treated with cobalt(III) acetate (2 equiv.) in acetic acid under argon. Three components were obtained by t.l.c. separation of the reaction mixture. ^{1}H N.m.r. and i.r. spectra showed that two of them were *threo*-(**2a**) and *erythro*-1,2-diacetoxy-1-(*p*-methoxyphenyl)propane (**3a**) and that the third component was a 1:1 mixture of 2-acetoxy-1-(*p*-methoxyphenyl)propan-1-ol and 1-acetoxy-1-(*p*-methoxyphenyl)propan-2-ol. Acetylation of the third component with sodium acetate and acetic anhydride gave (**2a**) and (**3a**), showing that it consists of *threo*-(**4a**) and *erythro*-2-acetoxy-1-(*p*-methoxyphenyl)propan-1-ol (**5a**), and *threo*-(**4a′**) and *erythro*-1-acetoxy-1-(*p*-methoxyphenyl)propan-2-ol (**5a′**).

In the light of these findings, the product distributions and isomer ratio of glycol monoacetates were determined by the method as described in the Experimental section.

Results of oxidation of (**1a**) and (**1b**) by cobalt(III) and manganese(III) acetate in acetic acid under various conditions are summarised in Table 1. All the reactions gave predominantly *threo*-glycols [(**4a**) + (**4a′**)] and *erythro*-isomer [(**5a**) + (**5a′**)] were always the minor products at 323 K. The same products were quickly obtained at 373 K but they were rapidly acetylated to the corresponding diacetates, which contained the *threo*- and *erythro*-isomers in a ratio of 1:1. The ratio of *threo*-glycol monoacetate [(**4a**) + (**4a′**)] to *erythro*-isomer [(**5a**) + (**5a′**)] also decreased gradually with temperature.

Table 1. Oxidation of anethole by cobalt(III) and manganese(III) acetate in acetic acid.

Entry No.	Substrate/ mmol	Oxidant/ mmol	Temp/ K	Time/ h	Yield[a] (%)	Product yields (mol%) (2a)	(3a)	(4a)	(5a)	(2a):(3a)	(4a):(5a)
1	(**1a**) (0.328)	Co(0.656)	313	2	97	8	6	79	7	1.3	11.3
2	(**1a**) (0.247)	Co(0.494)	373	0.833	94	16	16	56	13	1.0	4.3
3	(**1a**) (0.358)	Co(0.713)	373	0.5	91	44	42	7	7	1.0	1.0
4	(**1a**) (0.224)	Mn(0.448)	313	8	96	10	7	76	6	1.4	12.7
5	(**1a**) (0.243)	Mn(0.486)	373	0.333	99	16	16	47	21	1.0	2.2
6	(**1a**) (0.329)	Mn(0.658)	373	2	98	48	46	3	3	1.0	1.0
7	(**1b**) (0.219)	Co(0.438)	313	2	90	11	8	71	9	1.4	7.9
8	(**1b**) (0.101)	Mn(0.202)	313	8	97	15	8	68	9	1.9	7.6

[a] Total yield of (**2a**)–(**5a**).

Table 2. Oxidation of *E*- and *Z*-(unsubstituted and *p*-methylphenyl) propene by cobalt(III) and manganese(III) acetate in acetic acid in the presence of trifluoroacetic acid.

Entry No.	Substrate/ mmol	Oxidant/ mmol	TFA mmol	Temp/ K	Time/ h	Yield[a] (%)	Product yields (mol%) (2)	(3)	(4)	(5)	(2):(3)	(4):(5)
9	(**1c**) (0.328)	Co(0.656)	0	323	12	75	14	11	70	5	1.3	14
10	(**1c**) (0.261)	Mn(0.522)	1.4	323	17	53	11	5	71	13	2.2	5.3
11	(**1d**) (0.328)	Co(0.656)	0	323	12	40	23	16	57	4	1.4	14
12	(**1d**) (0.258)	Mn(0.525)	1.4	323	17	46	18	9	64	9	2.0	7.1
13	(**1e**) (0.331)	Co(0.662)	0	323	24	19	8	7	65	19	1.1	3.4
14	(**1e**) (0.331)	Co(0.662)	1.7	323	24	40	10	5	67	18	2.0	3.7
15	(**1e**) (0.288)	Mn(0.576)	1.4	323	24	48	7	2	72	18	3.5	4.0
16	(**1f**) (0.356)	Co(0.712)	1.8	323	24	26	29	16	46	9	1.8	5.1
17	(**1f**) (0.275)	Mn(0.549)	1.4	323	24	28	22	11	56	11	2.0	5.1

[a] Total yield of (**2**)–(**5**).

Oxidation of 1-(p-*Methylphenyl)propene.*—Oxidation of (*E*)-(**1c**) and (*Z*)-1-(*p*-methylphenyl)propene (**1d**) by cobalt(III) acetate (2 equiv.) in acetic acid under argon gave a mixture of *threo*-2-acetoxy-1-(*p*-methylphenyl)propan-1-ol (**4c**), *threo*-1-acetoxy-1-(*p*-methylphenyl)propan-2-ol (**4c′**), *erythro*-2-acetoxy-1-(*p*-methylphenyl)propan-1-ol (**5c**), and *erythro*-1-acetoxy-1-(*p*-methylphenyl)propanol-2-ol (**5c′**), as the main products at 323 K. At the same time, small amounts of *threo*-(**2c**), *erythro*-1,2-diacetoxy-1-(*p*-methylphenyl)propane (**3c**), and *p*-methylcinnamyl acetate (**6c**) were obtained at this temperature.

Manganese(III) acetate oxidation of (**1c**) and (**1d**) was too slow to examine product distribution. For example, only 7.6% of the substrate was consumed at 323 K over 48 h in acetic acid. Thus, the reaction was carried out in acetic acid containing trifluoroacetic acid (TFA) in order to accelerate the reaction. The same products as those obtained from cobalt(III) acetate oxidation were obtained in these reactions, except for the lack of formation of allylic oxidation product (**6c**) under these conditions.

The results of cobalt(III) and manganese(III) acetate oxidation of (**1c**) and (**1d**) are summarised in Table 2. In both oxidations, the ratio of *threo*-derivatives to *erythro*-isomer [(**4c**) + (**4c′**)]:[(**5c**) + (**5c′**)] in glycol monoacetates obtained from (**1c**) was nearly the same as those from (**1d**) at 323 K. The yields of diacetates, (**2c**) and (**3c**), increased with temperature at the expense of the monoacetates and the ratio of (**2c**):(**3c**) was close to unity.

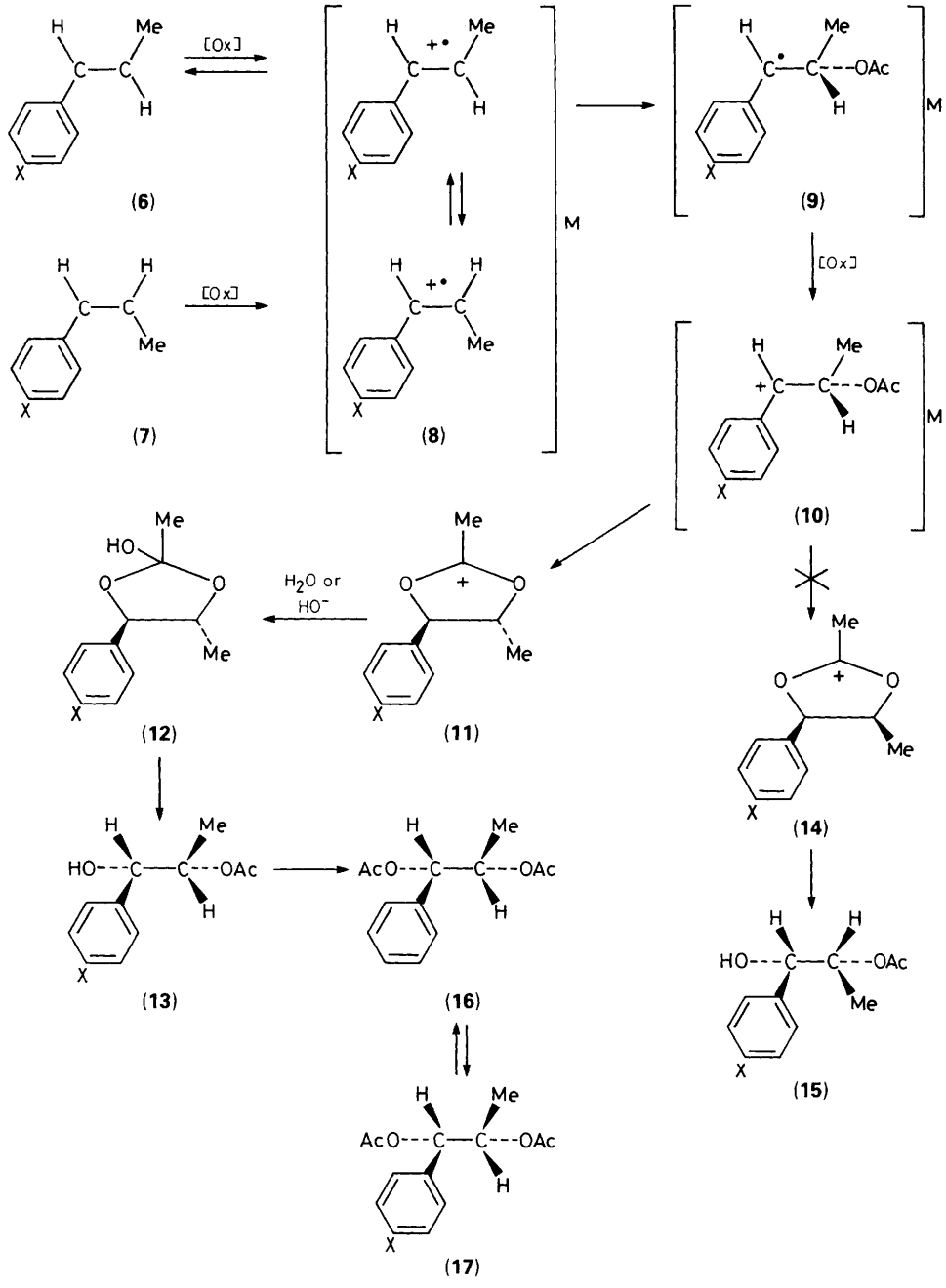
Oxidation of β-*Methylstyrene.*—Oxidation of (*E*)-(**1e**) and (*Z*)-β-methylstyrene (**1f**) by cobalt(III) and manganese(III) acetate was conducted in acetic acid containing TFA, since the reactions in acetic acid were very slow. All the reactions gave a mixture of *threo*-2-acetoxy-1-phenylpropan-1-ol (**4e**), *threo*-1-acetoxy-1-phenylpropan-2-ol (**4e′**), *erythro*-2-acetoxy-1-phenylpropan-1-ol (**5e**), and *erythro*-1-acetoxy-1-phenylpropan-2-ol (**5e′**) as main products, together with *threo*-(**2e**), *erythro*-1,2-diacetoxy-1-phenylpropane (**3e**) and cinnamyl acetate (**6e**). The last compound was a major product in the acetic acid reaction as found in the previous paper,[13,17] but the formation was suppressed by the addition of TFA to the system.

The results are listed in Table 2. The reactions were much slower than those of *p*-Me and *p*-OMe derivatives. The ratio of *threo*:*erythro* in the glycol monoacetates was nearly the same in cobalt(III) and manganese(III) acetate oxidation of (**1e**) and (**1f**), although the values were much lower than those in oxidation of *p*-substituted compounds.

Reaction Mechanism.—In the oxidations of alkenes by lead(IV) acetate,[2] permanganate(VII),[18,19] osmium(VIII) tetraoxide[20,21] *etc.*, in which the reaction proceeds stereoselectively, different products were obtained from different geometries (*Z* to *erythro* and *E* to *threo*). Therefore, we were surprised that *threo*-glycol monoacetate [(**4a**) + (**4a′**)] was exclusively obtained from both (*Z*)-(**1b**) and (*E*)-anethole (**1a**) in cobalt(III) and manganese(III) acetate oxidation. Since the same results were obtained in oxidation of (**1c–f**), the behaviour is common for oxidation of alkenes by cobalt(III) and manganese(III) acetate.

This phenomenon may occur if *threo*-glycol monoacetates are thermodynamically much more stable than *erythro* isomers. However, it is difficult to predict the large difference in the stabilities between these compounds.[22] On the basis of these considerations, the exclusive formation of *threo*-diols from both *E*- and *Z*-alkenes must be attributed to the structure of an intermediate(or a transition state) favourable for the formation of the *threo*-diols.

We have already suggested a radical cation, radical, and



Scheme 3. M = metal ion.

carbocation co-ordinated to a cobalt(III) or cobalt(II) ion as an intermediate in the cobalt(III) acetate oxidation of alkenes in acetic acid.[14–17] The above stereochemical data may be explained by a combination of our previous mechanism with that of Prevost type reaction.[2,8,23]

The oxidation of a double bond by a one-electron oxidant may initially generate the corresponding radical cation followed by the addition of acetate ion (perhaps in the oxidant) to the radical cation to give an acetylated radical which is further oxidised to a cation. A series of the above reactions may occur in metal-co-ordinated complexes, since the product distribution is not disturbed by the addition of water, acetic anhydride, sodium acetate, nor copper(II) acetate *etc.* to the reaction mixture as reported previously.[14] Substituents attached to carbons derived from parent double bonds freely rotate in these co-ordinated intermediates.

The carbonyl oxygen of the acetyl group in the carbocation intermediate (**10**) may give a five-membered acetoxonium ion (**11**) or (**14**) by intramolecular attack of the cationic carbon. The addition of hydroxy group (perhaps from the oxidant) followed by ring opening gave the corresponding glycol monoacetate. Since the substituents in the five-membered ring are almost eclipsed, there is considerable torsional strain. Thus, the acetoxonium ion (**14**) with phenyl and methyl groups on one side is much more unstable than (**11**) which has them on both sides. Therefore, the acetoxonium ion (**11**) may be exclusively formed in ring closure. Since the intermediate is known to be converted into the glycol monoacetate holding geometry, *threo*-glycol derivatives were formed exclusively.

A similar acetoxonium ion is proposed in order to explain the stereospecific formation of glycol derivatives in the oxidation of alkenes by lead(IV) acetate,[2] Prevost reaction,[8] and the

Woodward hydroxylation method of alkene.[23] It is reported in these reactions that the acetoxy group and the residue (lead triacetate in the former case and halogen in the latter two cases) add to the double bond in an *anti* manner and then the carbonyl oxygen in the acetyl group attacks the neighbouring carbon atom from the rear of the residue to generate the corresponding five-membered acetoxonium ion [(**11**) from *E*-alkene and (**14**) from *Z*-alkene]. Therefore, the intermediate from *E*-alkene is different from that from the *Z*-isomer. On the other hand, only (**11**), which is more stable than (**14**), may be formed at low temperature in the present reaction, since there is no strong bond interaction between cationic carbon and ligand metal in (**10**), resulting in the exclusive formation of *threo*-glycol monoacetates.

The glycol monoacetate formed was acetylated in acetic acid during the oxidation to give the corresponding diacetate, which consisted of almost identical amounts of *threo*- and *erythro*-isomer. Since equal amounts of (**2a**) and (**3a**) were obtained in the treatment of isolated glycol monoacetate [(**4a**) + (**4a′**)] containing [(**5a**) + (**5a′**)] (8%) in the presence and absence of sodium acetate at 373 K for 30 min, stereospecificity may be lost in the acetylation step of glycols. The mechanism is still uncertain but it is expected that the acetylation proceeded through an S_N1-type substitution or that S_N2-type substitution occured freely in the products.

When (**1b**) was treated with cobalt(III) or manganese(III) acetate, the content of (**1a**) in recovered substrate was higher than that in the original one. Since the consumption of (**1a**) by these oxidants is as fast as or slightly faster than that of (**1b**), an increase in (**1a**) is not attributable to the concentration of (**1a**) contaminating the starting material, (**1b**) but to isomerization of (**1b**) to (**1a**) catalysed by these metal oxidants. No isomerization of (**1b**) to (**1a**) could be observed in acetic acid under comparable conditions in the absence of cobalt(III) or manganese(III) acetate. These results may show that the first one-electron transfer step from alkene to oxidant is a reversible process, supporting a free rotation about C–C single bond in the intermediate. Similar isomerization of *Z*-alkene to the *E*-isomer was found in the cobalt(III) and manganese(III) acetate oxidation of stilbene.[24]

Conclusions

In conclusion, oxidation of alkenes by one-electron oxidants [cobalt(III) and manganese(III) acetate] proceeds through a metal-co-ordinated radical cation, radical, and carbocation and the stereochemistry of the products is determined by the thermodynamic stability of the intermediate. This mechanism is very different from those involving lead(IV) acetate, permanganate, and osmium(VIII) tetraoxide oxidations of alkenes.

Experimental

^{1}H N.m.r. spectra were measured in CCl_4 on a JEOL JNM-PMX60 n.m.r. spectrometer. I.r. (NaCl) spectra were recorded on a JASCO A-100 spectrophotometer. Gas chromatography was carried out on a Shimadzu GC-4CM instrument with a 2 m glass column packed with 1.5% Silicone OV-17 on Chromosorb W, with temperature programmed from 353–473 K. For measurements of product yield, biphenyl or benzophenone was used as an internal standard. Preparative g.l.c was carried out on a Shimadzu GC-4A instrument connected to a fraction collector through a heated tube, with a 2 m stainless column packed with 30% PEG-20M on Celite 545.

Reagents.—Cobalt(III)[25,26] and manganese(III)[27] acetate were prepared by known methods. (*E*)-Anethole (**1a**) and (*E*)-β-methylstyrene (**1e**) were commercial products and were used without further purification. (*E*)-1-(*p*-Methylphenyl)propene (**1c**) was prepared by reduction of *p*-methylpropiophenone ($NaBH_4$) in methanol–water followed by dehydration ($KHSO_4$) under reduced pressure and was purified by a preparative g.l.c. (*Z*)-β-Methylstyrene (**1f**) was prepared by reduction of phenylpropyne by $NaBH_4$ and BF_3 etherate and purified by a preparative g.l.c. (*Z*)-Anethole (**1b**) was prepared as follows. U.v. light (100 W high-pressure mercury lamp) was used to irradiate a solution of (**1a**) (*ca.* 2 g) and benzil (0.02 g) as a catalyst in acetonitrile (150 cm^3) for 9 h at room temperature. After evaporation of the acetonitrile, the product was distilled under reduced pressure (378–379 K/16 mmHg). The compound was purified by a preparative g.l.c. (*Z*)-1-(*p*-Methylphenyl)-propene (**1d**) was prepared from (**1c**) as described for (*Z*)-anethole except that ether was used as solvent. These alkenes were identified by their ^{1}H n.m.r. and i.r. spectra.

Oxidation Procedure.—A typical procedure was as follows: a weighed amount of alkene was mixed with cobalt(III) or manganese(III) acetate in acetic acid (5 cm^3) in a flask equipped with a glass stopper. The flask was flushed with dry argon gas and then kept at constant temperature without agitation. After addition of an internal standard, the solution was poured into brine (*ca.* 30 cm^3) and extracted with ether (3 × 10 cm^3). The combined ethereal solution was washed successively with brine, aqueous Na_2CO_3(10%), and brine, and dried (Na_2SO_4). After filtration, the ether was removed using a rotary evaporator to leave a pale-yellow oil, which was analysed by g.l.c.

The resultant oil was acetylated with anhydrous NaOAc (five-fold amount of the oil) and acetic anhydride (4 cm^3) for 2–4 h at 373 K. The same work-up as described above, except for the addition of an internal standard, gave a pale-yellow oil, which was analysed by g.l.c.

Reaction products were identified from their g.l.c. retention times.

Reference Compounds.—*threo*-1-Arylpropane-1,2-diol diacetates were obtained by oxidation of the corresponding alkenes with cobalt(III) and/or manganese(III) acetate. *erythro* Derivatives were prepared by treatment of the alkenes with persulphate in acetic acid,[22] since cobalt(III) and manganese(III) acetate oxidations gave low yields of *erythro*-isomer.

Oxidation of (E)-*Anethole* (**1a**) *with Manganese*(III) *Acetate.*—(*E*)-Anethole (0.5 g) was treated with manganese(III) acetate (1.85 g, 2 equiv.) in acetic acid (30 cm^3) for 4 h at 323 K under argon. The solution was poured into brine (150 cm^3) and extracted with ether (3 × 50 cm^3). The combined ethereal solution was washed successively with brine, 10% aqueous Na_2CO_3, and brine, and dried (Na_2SO_4). After filtration, the ether was removed under reduced pressure to afford a pale-yellow oil. The oil was separated by t.l.c. using silica gel and hexane–ethyl acetate (4:1) to give a mixture of glycol monoacetates [(**4a**), (**4a′**), (**5a**), and (**5a′**)]. δ_H (solvent CCl_4) 7.12 (2 H, d), 6.71 (2 H, d), 5.31 (0.5 H, d, *J* 7.6 Hz), 4.37 (0.5 H, d, *J* 7.2 Hz), 4.82 (0.5 H, m), 3.87 (0.5 H, m), 3.73 (3 H, s), 2.60 (1 H, broad), 1.98 (3 H, s), 1.01 (1.5 H, d), and 0.91 (1.5 H, d). ν_{max} (liquid film, NaCl) 3 450, 3 000, 2 960, 1 740, 1 620, 1 520, and 1 250 cm^{-1}.

The glycol monoacetates were acetylated with anhydrous sodium acetate (1.9 g) and acetic anhydride (5 cm^3). A work-up similar to that described above gave an oil, which was separated by t.l.c. using silica gel and hexane–ethyl acetate (9:1) to give (**2a**). *threo*-1-(*p*-Methoxyphenyl)propane-1,2-diol diacetate (**2a**): δ_H (CCl_4) 7.15–6.72 (4 H, q), 5.57 (1 H, d, *J* 7.6 Hz), 5.10 (1 H, m), 3.70 (3 H, s), 1.97 (3 H, s), 1.93 (3 H, s), and 1.02 (3 H, d).

ν_{max}(liquid film) 3 005, 2 960, 1 750, 1 620, 1 520, 1 380, and 1 250 cm^{-1}.

A mixture of glycol monoacetates [(**4a**), (**4a′**), (**5a**), and (**5a′**)] and diacetate (**2a**) were obtained by reaction of (**1a**) with cobalt(III) acetate in acetic acid and by the same work-up as described above.

erythro-1-(*p*-Methoxyphenyl)propane-1,2-diol diacetate (**3a**) was prepared by treating (**1a**) with persulphate in acetic acid.[22] The same work-up as described in the case of the *threo* isomer gave an oil. T.l.c. separation of the oil using silica gel and hexane–ethyl acetate (9:1) gave (**3a**) in addition to (**2a**). *erythro*-1-(*p*-Methoxyphenyl)propane-1,2-diol diacetate (**3a**). δ_H (CCl_4). 7.02–6.73 (4 H, q), 5.75 (1 H, d, *J* 4 Hz), 5.07 (1 H, m), 3.75 (3 H, s), 2.05 (3 H, s), 1.93 (3 H, s), and 1.12 (3 H, d). ν_{max}(liquid film) 3 000, 2 950, 1 740, 1 520, 1 370, and 1 250 cm^{-1}.

Oxidation of (E)-1-(p-*Methylphenyl)propene* (**1c**) *with Manganese*(III) *Acetate in Acetic Acid Containing* TFA.—Substrate [(**1c**), 0.58 g] was treated with cobalt(III) acetate (0.22 mol dm^{-3}, 40 cm^3, 2 equiv.) for 4 h at 373 K under argon. The same work-up as above gave an oil, which was acetylated with anhydrous sodium acetate (2.5 g) and acetic anhydride (25 cm^3). The same work-up and t.l.c. separation under the same conditions as above gave (**2c**). *threo*-1-(*p*-Methylphenyl)propane-1,2-diol diacetate (**2c**): δ_H (CCl_4) 7.07 (4 H, s), 5.57 (1 H, d *J* 7.6 Hz), 5.08 (1 H, m), 2.28 (3 H, s), 1.97 (3 H, s), 1.94 (3 H, s), and 0.98 (3 H, d). ν_{max} (liquid film) 3 000, 2 950, 1 740, 1 370, 1 220, and 1 020 cm^{-1}.

erythro-1-(*p*-Methylphenyl)propane-1,2-diol diacetate (**3c**) was prepared at 353 K using the same method as that for(**3a**): δ_H (CCl_4) 7.08 (4 H, s), 5.78 (1 H, d, *J* 4 Hz), 5.07 (1 H, m), 2.32 (3 H, s), 2.05 (3 H, s), 1.92 (3 H, s), and 1.11 (3 H, d). ν_{max} (liquid film) 3 000, 2 950, 1 740, 1 370, and 1 225 cm^{-1}.

Oxidation of (E)-β-*Methylstyrene* (**1e**) *with Manganese*(III) *Acetate*.—Alkene [(**1e**), 0.46 g] was treated with manganese(III) acetate (2.2 g, 2 equiv.) in acetic acid containing TFA (8.9 g) for 6 h at 323 K. The same work-up as described above gave an oil, which was acetylated with sodium acetate (2.5 g) and acetic anhydride (25 dm^3) for 2 h at 373 K. The same work-up and separation by t.l.c. gave a pale-yellow oil (**2e**). *threo*-1-Phenylpropane-1,2-diol diacetate (**2e**): δ_H (CCl_4) 7.21 (5 H, s), 5.58 (1 H, d, *J* 7 Hz), 5.11 (1 H, m), 2.00 (3 H, s), 1.93 (3 H, s), and 1.04 (3 H, d). ν_{max} (liquid film) 3 040, 2 990, 1 740, 1 370, and 1 220 cm^{-1}.

erythro-1-(*p*-Phenyl)propane-1,2-diol diacetate (**1f**) was prepared by the same method as that for other *erythro*-isomers: δ_H (CCl_4) 7.23 (5 H, s), 5.83 (1 H, d, *J* 4 Hz), 5.07 (1 H, m), 2.07 (3 H, s), 1.93 (3 H, s) and 1.18 (3 H, d). ν_{max} (liquid film) 3 000, 2 950, 1 750, 1 370, 1 230, and 1 030 cm^{-1}.

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