Oxidation by Cobalt(III) Acetate. Part 11.[1] Oxidation of Conjugated Dienes by Cobalt(III) Acetate in Acetic Acid

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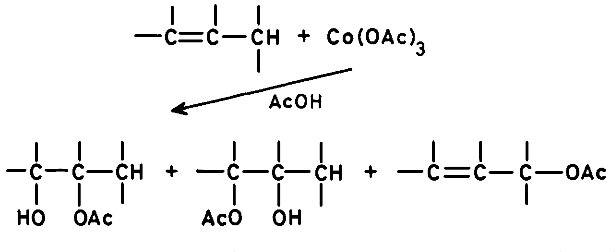
The oxidation of aliphatic and aromatic conjugated dienes by cobalt(III) acetate in acetic acid has been investigated. Open chain dienes were smoothly oxidized by cobalt(III) acetate to give *vic*-diol derivatives. Cyclo-octadiene was slowly converted into allylic acetate by the oxidant. The reaction mechanism is discussed in terms of a Co-co-ordinated radical cation.

Oxidation of alkenes by cobalt(III) acetate in acetic acid is found to give allylic acetates and glycol monoacetates, the product ratios of which depend on the structure of the olefins;[1,2] *e.g.*, oxidation of aliphatic alkenes gave exclusively and regioselectively allylic acetates,[3,4] whereas aromatic olefins gave glycol monoacetates and allylic acetates.[5,6]



Expansion of our interests has led us to examine the oxidation of conjugated dienes by the oxidant, since this may yield 1,4- and 1,2-addition products and allylic acetates, and product analysis may provide an intermediate of the cobalt(III) acetate oxidation. There are several reports on the oxidation of conjugated dienes by a variety of metallic oxidants.[7–15] These reactions generally give 1,2-addition products, especially 1,2-diol derivatives,[7,9–13] and 1,4-addition products.[14,15] However, there is no report on the oxidation of dienes by one-electron metallic oxidants with the exception of manganese(III) acetate,[8] which self-decomposes to give a carboxymethyl radical. In this report, we describe the products and the reaction mechanism of the oxidation of conjugated dienes by cobalt(III) acetate in acetic acid.

Results and Discussion

The reaction was carried out under nitrogen and the products were isolated from the reaction mixture by thin-layer chromatography (t.l.c.). The products were identified by n.m.r. and i.r. spectra or by a combination of these methods with a chemical method. The results are summarized in the Table.

Oxidation of butadiene and heptadiene gave complex mixtures and material balance was very poor, possibly due to the slow reactions and volatility of these compounds. Hence, the product study was carried out using higher analogues of these dienes. The oxidation of 2,5-dimethylhexa-2,4-diene (**1a**) by cobalt(III) acetate in acetic acid gave only 1,2-addition products, a mixture of 2-acetoxy-2,5-dimethylhex-4-en-3-ol and 3-acetoxy-2,5-dimethylhex-4-en-2-ol (**2a**), in good yield. The compounds were identified by ^1H and ^{13}C n.m.r. spectra. However, the spectra were considerably complicated since the products were a mixture of (**2a**) and (**2b**). Hence, they were acetylated using acetic anhydride and sodium acetate at 373 K for 24 h, since it was expected that both compounds would be converted into the same compound (4,5-diacetoxy-2,5-dimethylhex-2-ene), which was identified by ^1H and ^{13}C n.m.r. spectra. 1,4-Diol derivatives and allylic oxidation product were not found as products by these spectra. G.l.c. analysis also confirmed that the use of an excess of oxidant gave the products in 98% yield and that no 1,4-addition product and allylic oxidation product were formed.

A series of 1-phenylbutadienes, which have hydrogen, methyl, ethyl, isopropyl, and phenyl substituents at the end opposite the phenyl group on the butadiene skeleton, was treated with cobalt(III) acetate in order to study the general mechanism of the oxidation of the dienes by the oxidant. *vic*-Diol derivatives were obtained in all cases, but which double bond in the diene was converted could not be specified by n.m.r. and i.r. spectra for substrates (**1b**) and (**1d—f**). Hence, the products were hydrolysed by aqueous sodium hydroxide to give diols, which were then oxidized by cobalt(III) acetate in acetic acid. Obtained products were identified by their n.m.r. and i.r. spectra and also by comparison of the g.l.c. retention times of the products with those of authentic samples. The latter included cinnamaldehyde for all substrates except (**1c**), for which cinnamaldehyde and benzaldehyde were detected in nearly equal amounts. Thus, the products of the cobalt(III) acetate oxidation of dienes were confirmed to be *vic*-diol derivatives in which the double bonds adjacent to the phenyl groups remained unchanged.

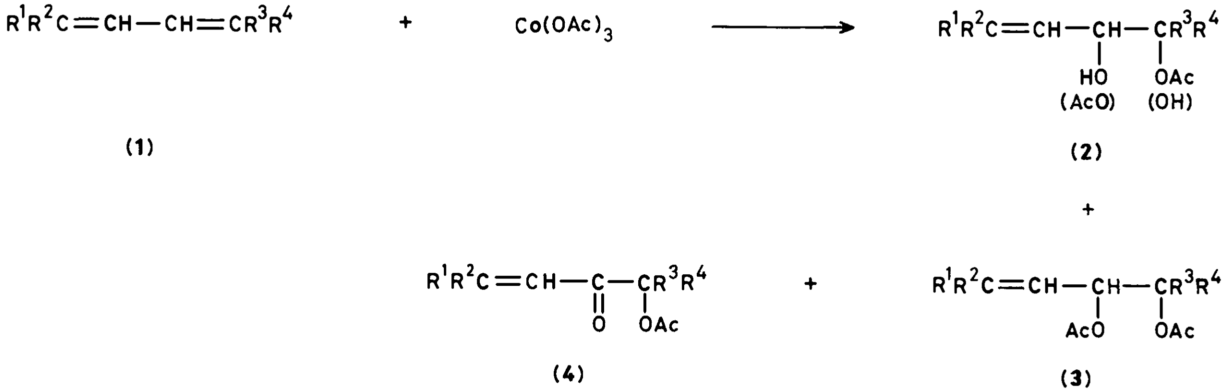
Cobalt(III) acetate oxidation of some olefins, at the first stage, gives the corresponding hydroxy acetates, which are then gradually acetylated. Thus, hydroxy acetates may be obtained from short reaction periods while the diacetate results from longer periods. In the present study, the oxidations of (**1a**) and (**1c**) were stopped between 1—3 h, but the oxidations of (**1b**) and (**1d—f**) required 6 h for enough conversion of the substrates. Thus, diacetates were formed in the latter cases and not in the former cases. It is difficult to explain the formation of 1-acetoxy-4-phenylbut-3-en-2-one (**4b**) only in the oxidation of (**1b**). However, it may be rationalized in terms of the electrosteric requirements of the oxidant since the oxidation is reported to be strongly affected by steric factors.[3,4,16] The bulky oxidant, cobalt(III) acetate, may attack the hydroxy group of the hydroxy acetate derived from (**1b**) since it has no substituent at the C-4 position. On the other hand, the oxidant cannot approach the hydroxy group in the cases of the other olefins because of steric repulsion betwen the C-4 substituents and the oxidant.

The oxidation of cyclo-octadiene by the oxidant led to the

Table. Oxidation of conjugated dienes by cobalt(III) acetate[a] in acetic acid

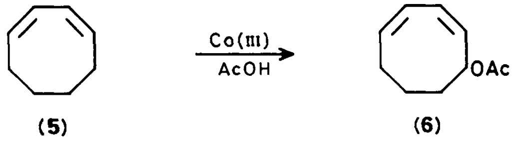
Substrate	Co(III)/Diene	Time/h	Temp./K	Yield (mol %)			
				(1)	**(2)**	**(3)**	**(4)**
(1a)	2	1	303	18	71	0	0
	2	2	303	15	78	0	0
	4	2	303	1	98	0	0
Cyclo-octa-1,3-diene	2	6	333	30	52[b]	—	—
	4	6	333	14	65[b]	—	—
	2	6	353	17	41[b]	—	—
(1b)	4	6	323	0	36	24	22
(1c)	2	3	333	0	57	Trace	0
(1d)	2	6	333	0	32	37	0
(1e)	2	6	313	0	29	39	0
(1f)	2	6	313	0	34	26	0

[a] $[Co(OAc)_3]$ 0.246M. [b] Cyclo-octa-2,4-dienyl acetate.



a; $R^1 = R^2 = R^3 = R^4 = Me$, **b**; $R^1 = Ph$, $R^2 = R^3 = R^4 = H$, **c**; $R^1 = R^3 = Ph$, $R^2 = R^4 = H$,
d; $R^1 = Ph$, $R^2 = R^3 = H$, $R^4 = Me$, **e**; $R^1 = Ph$, $R^2 = R^3 = H$, $R^4 = Et$,
f; $R^1 = Ph$, $R^2 = R^3 = H$, $R^4 = Pr^i$

formation of the allylic oxidation product, cyclo-octa-2,4-dienyl acetate at a slower rate than those of the open-chain dienes. No 1,2- and 1,4-addition products were detected by g.l.c. analysis. The prolonged reaction and the addition of strong acid (trifluoroacetic acid) resulted in the decreased yield of the allylic acetate. This result may be specific to the oxidation of the cyclooctadiene because the aliphatic diene (**1a**) gave only the corresponding *vic*-diol derivatives.



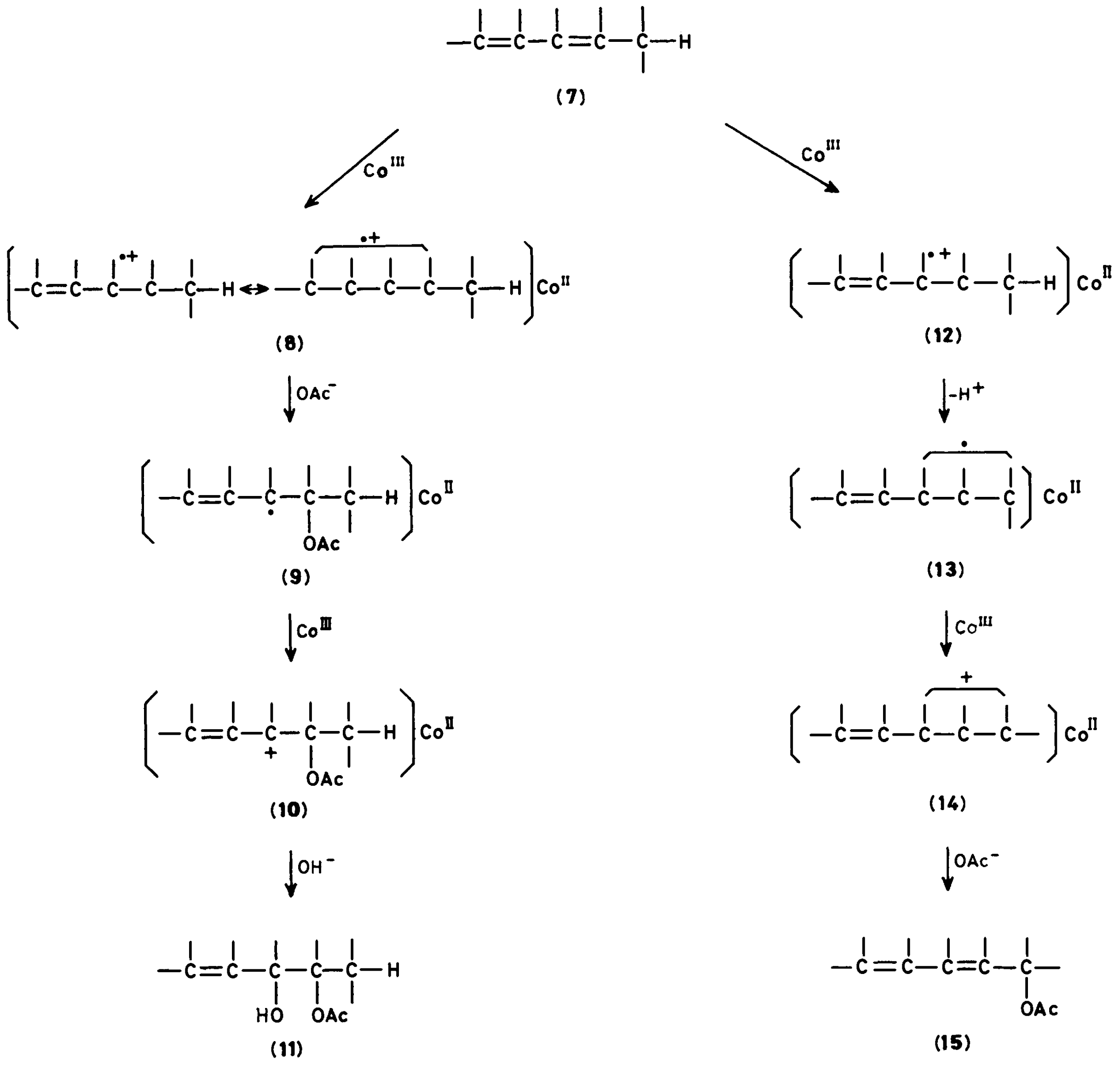
(5) **(6)**

On the basis of the above results, we conclude that cobalt(III) acetate oxidation of conjugated dienes gave only 1,2-addition products across the double bond, although a further oxidation product was observed in one case. Selectivity of the product was not effected by the R^4 substituents of the 1-phenylbutadienes. The exclusive formation of 1,2-adducts and the absence of allylic acetate may indicate that increased conjugation favours the formation of glycol derivatives.

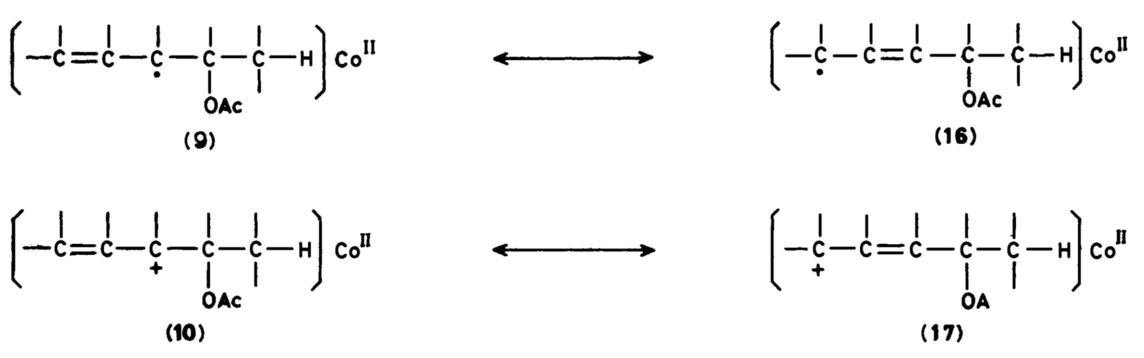
Absence of 1,4-addition adducts may show that the radical cation (**8**), radical (**9**), or carbocation (**10**) intermediates involved during the reaction are not independent species. A positive charge and/or an unpaired electron on the radical must be localized on two carbon atoms in these intermediates, since if they are delocalized over the diene, 1,4- and 1,2-addition adducts should be obtained.[17] We have already suggested the involvement of a Co-co-ordinated intermediate in the oxidation of alkenes by cobalt(III) acetate in order to explain the regioselective formation of methyl-substituted cyclohexenyl acetates,[3] some steric retention for the formation of glycol monoacetates from *cis*- and *trans*-β-methylstyrenes, and the absence of formation of the rearrangement product for asymmetrical olefins.[18] The formation of 1,2-diol derivatives in this work may be rationalized in terms of this Co-co-ordinated intermediate.

We now propose the reaction mechanism described in Scheme 1, on the basis of these observations.

One-electron transfer from the double bond to the oxidant gives a Co-co-ordinated radical cation (**8**). The radical cation (**8**) is attacked by acetate ion (may be the acetoxy ligand of the cobalt salt) to form radical (**9**), which is then oxidized by a second cobalt(III) acetate to give carbocation (**10**) followed by the addition of acetate or hydroxide ion [acetoxy or hydroxy ligand of cobalt(III) acetate]. The sequence of these reactions must take place *via* the Co-co-ordinated complex as illustrated



Scheme 1.



Scheme 2.

in the reaction mechanism, since only 1,2-diol derivatives and their further oxidation products are obtained.

Intermediates (**9**) and (**10**) have structures similar to those in the allylic oxidations of olefins by cobalt(III) acetate.[3,4] Since allylic acetate, in which the double bond in the original olefin remained unmoved, is predominant in the oxidation of aliphatic olefins,[3] (**9**) and (**10**) may be favourable structures rather than (**16**) and (**17**), which favour the 1,4-addition reaction, perhaps due to the co-ordination of cobalt ion in the oxidation of dienes by cobalt(III) acetate. Therefore, 1,2-addition may be predominant in the oxidation of dienes, unless the two double bonds in the diene are isolated from each other. It is, however, difficult to explain why (**9**) and (**10**) are more stable than (**16**) and (**17**), respectively, since it cannot be expected that there is large difference in energy between these two structues. Further study is necessary in order to clarify this problem.

In the oxidation of cyclo-octadiene (**5**), on the other hand, the mechanism may be different from that of substrates (**1a**—**f**). The cyclic diene adopts a crown shape, in which the two double bonds cannot be fully conjugated with each other because of steric requirements. Thus, it would behave as if it were an aliphatic olefin, which is oxidized by cobalt(III) acetate to give the allylic acetate. In other words, cobalt(III) acetate attacks one of the double bonds to give the olefinic radical cation (**12**). When the substrate is an aliphatic olefin, the resultant radical cation (**12**) has a tendency to split off a proton to give a radical (**13**), followed by oxidative acetoxylation.

Experimental

^{1}H N.m.r. spectra were measured for solutions in CCl_4 or $CHCl_3$ on a JEOL model PMX-60 spectrophotometer. I.r. spectra were recorded for thin films on a JASCO spectrophotometer. G.l.c. was carried out on a Shimadzu GC-6A instrument with temperature programming using a 2 m glass column packed with 5% PEG-20M on Chromosorb WAW-DMCS. For the determination of yields an internal standard was used. Preparative g.l.c. was performed on a Shimadzu GC-4A instrument with a 2 m stainless steel column packed with 30% PEG-20M on Celite 545, attached to a Shimadzu APP-5 fraction collector through a heated glass joint.

2,5-Dimethylhexa-2,4-diene (**1a**), cyclo-octa-1,3-diene (**5**), and *trans,trans*-1,4-diphenylbuta-1,3-diene (**1c**) were commercially available and were used without further purification. *trans*-1-Phenylbuta-1,3-diene (**1b**) was prepared by dehydration, over $KHSO_4$, of 4-phenylbut-3-en-2-ol,[19] which was prepared by the lithium aluminium hydride reduction of benzylidene acetone. 1-Phenylpenta-1,3-diene (**1d**), 1-phenylhexa-1,3-diene (**1e**), and 5-methyl-1-phenylhexa-1,3-diene (**1f**) were prepared by Wittig reaction[20] from cinnamaldehyde and the corresponding triphenylphosphonium salts.[21,22] The purities of these compounds were satisfactory by g.l.c. analysis (over 98% in the ratio of peak area of gas chromatogram) and the structures were determined by n.m.r. spectra. Cobalt(III) acetate was prepared by bubbling ozone into acetic acid solution containing cobalt(II) acetate tetrahydrate and acetic anhydride.[23]

Oxidation Procedures.—Substrate (*ca*. 0.5 g) was mixed with cobalt(III) acetate solution (0.24 mol dm^{-3}) in a flask. After flushing with nitrogen or argon, the flask was immersed in a thermostat kept at constant temperature for a given period. The mixture was poured into brine and extracted (× 3) with ether. The combined ether extracts were washed successively with brine, 20% aqueous sodium carbonate, and brine, and then dried over anhydrous Na_2SO_4. After filtration, the ether was removed on a rotary evaporator under reduced pressure to leave a pale yellow oil, which was analysed by g.l.c. or purified by chromatography. For gas chromatographic determination of the product yields, a suitable internal standard was added just before work-up.

Oxidation of 2,5-*dimethylhexa*-2,4-*diene* (**1a**). The product obtained by the method described above was isolated by t.l.c. (silica gel; hexane–ethyl acetate 8:2). The structure of the product was determined by n.m.r. spectroscopy and was found to be a mixture of 2-acetoxy-2,5-dimethylhex-4-en-3-ol and 3-acetoxy-2,5-dimethylhex-4-en-2-ol (**2a**), which could not be separated even by g.l.c. analysis; $\delta_H(CCl_4)$ 1.2 (6 H, s), 1.7 (6 H, s), 2.0 (3 H, s), 5.1 (1 H, 2 pairs of doublets), and 5.4 (1 H, 2 pairs of doublets), (hydroxy peak was broad and could not be identified); $\delta_C(CDCl_3)$ (off resonance) 170.3(s), 139.0(s), 120.1(d), 103.4(d), 77.0(d), 72.1(s), 63.5(s), 25.8(s), 25.6(s), and 24.2—15.0 (5 peaks); $\nu_{max.}$(film) 3 420, 1 750, and 1 270 cm^{-1}. The compounds were further identified by acetylation. The mixture was treated with acetic anhydride and sodium acetate in a flask at 373 K for 24 h. The same work-up as described above gave a colourless oil, which was chromatographed to give the corresponding diacetate (4,5-diacetoxy-2,5-dimethylhex-2-ene); $\delta_H(CDCl_3)$ 5.80 (1 H, d), 5.15 (1 H, d), 2.05 (3 H, s), 2.00 (3 H, s), 1.80 (6 H, s), and 1.45 (6 H, s); $\delta_C(CDCl_3)$ (off resonance) 139.3(s), 118.7(d), 82.2(s), 74.0(d), and 25.4—18.1 (6 peaks); $\nu_{max.}$(film) 3 000, 2 950, 1 740, and 1 250 cm^{-1}. The yield (98%) was determined by g.l.c. analysis using an internal standard.

Oxidation of cyclo-octa-1,3-*diene* (**5**). The crude product was purified by t.l.c. (silica gel; hexane–ethyl acetate 8:2) to give cyclo-octa-2,4-dienyl acetate (**6**); $\delta_H(CCl_4)$ 1.5—2.3 (6 H, m), 2.0 (3 H, s), and 5.4—6.0 (5 H, m); $\nu_{max.}$(film) 1 730 and 1 240 cm^{-1}. The yield was determined by g.l.c. analysis using an internal standard.

Oxidation of trans-1-*phenylbuta*-1,3-*diene* (**1b**). The crude mixture was separated by t.l.c. (silica gel; hexane–ethyl acetate 8:2) to give three compounds: 1-acetoxy-4-phenylbut-3-en-2-ol (**2b**); $\delta_H(CCl_4)$ 2.2 (3 H, s), 2.7 (1 H, br), 4.2 (2 H, d), 5.5 (1 H, m), 6.1 (1 H, m), 6.7 (1 H, d), and 7.2—7.5 (5 H, m); $\nu_{max.}$(film) 3 400, 1 720, 1 240, and 960 cm^{-1}. 1-Acetoxy-4-phenylbut-3-en-2-one (**4b**); $\delta_H(CCl_4)$ 2.2 (3 H, s), 4.9 (2 H, s), 6.7 (1 H, d), 7.2—7.5 (5 H, m), and 7.6 (1 H, d); $\nu_{max.}$(film) 1 740, 1 690, 1 230, and 975 cm^{-1}. 1,2-Diacetoxy-4-phenylbut-3-ene (**3b**): $\delta_H(CCl_4)$ 2.0 (6 H, s), 4.2 (2 H, d), 5.6 (1 H, m), 6.0 (1 H, m), 6.6 (1 H, d), and 7.2—7.5 (5 H, m); $\nu_{max.}$(film) 1 750, 1 250, and 980 cm^{-1}. It was found by g.l.c. analysis that treatment of 1-acetoxy-4-phenylbut-3-en-2-ol (**2b**) with cobalt(III) acetate in acetic acid gave the corresponding ketone 1-acetoxy-4-phenylbut-3-en-2-one (**4b**) in about 50% yield.

Oxidation of trans,trans-1,4-*diphenylbuta*-1,3-*diene* (**1c**). Treatment of the diene with cobalt(III) acetate in acetic acid under nitrogen followed by separation as described above gave the corresponding diol monoacetate (**2c**) in 57% yield with a trace of diol diacetate (**3c**). These compounds were identified as follows: the diol monoacetate (**2c**) was refluxed in a mixture of 10% aqueous sodium hydroxide (50 ml) and methanol (10 ml) for 2 h followed by oxidation of the resultant diol by cobalt(III) acetate, to give benz- and cinnam-aldehyde in almost equal amounts. Acetylation of the 1,2-diol monoacetate by sodium acetate and acetic anhydride gave the 1,2-diol diacetate. 1-Acetoxy-1,4-diphenylbut-3-en-2-ol (**2c**): $\delta_H(CCl_4)$ 2.1 (3 H, s), 5.4—6.8 (4 H, m), and 7.1—7.3 (10 H, m); $\nu_{max.}$(film) 3 400, 1 710, and 1 220 cm^{-1}.

Oxidation of 1-*phenylpenta*-1,3-*diene* (**1d**). 1-Phenylpenta-1,3-diene (**1d**) was treated with cobalt(III) acetate in acetic acid under argon at 333 K for 6 h. After work-up described above, the mixture was chromatographed to give two products. A mixture of 3-acetoxy-5-phenylpent-4-en-2-ol and 4-acetoxy-1-phenylpent-1-en-3-ol (**2d**): $\delta_H(CCl_4)$ 1.2 (3 H, d), 1.9—2.1 (total 3 H, a pair of singlets), 2.6—3.1 (1 H, br), 3.8—4.4 (1 H, m), 4.7—5.3 (1 H, m), 5.8—6.8 (2 H, m), and 7.2 (5 H, s); $\nu_{max.}$(film) 3 450, 1 730, 1 240, and 970 cm^{-1}. 3,4-Diacetoxy-1-phenylpent-1-ene (**3d**): $\delta_H(CCl_4)$ 1.2 (3 H, d), 1.8—2.1 (6 H, a pair of singlets), 4.9—6.8 (4 H, m), and 7.2 (5 H, s); $\nu_{max.}$(film) 1 740, 1 230, and 970 cm^{-1}.

Oxidation of 1-*phenylhexa*-1,3-*diene* (**1e**). Treatment of the diene as described above gave two products. A mixture of 3-acetoxy-1-phenylhex-1-en-4-ol and 4-acetoxy-1-phenylhex-1-en-3-ol (**2e**): $\delta_H(CCl_4)$ 0.8 (3 H, t), 1.2—1.7 (2 H, m), 1.9—2.0 (total 3 H, a pair of singlets), 3.4—3.8 (1 H, br), 4.0—5.3 (2 H m), 5.7—6.7 (2 H, m), and 7.2 (5 H, s); $\nu_{max.}$(film) 3 450, 1 730, 1 240, and 970 cm^{-1}. 3,4-Diacetoxy-1-phenylhex-1-ene (**3e**): $\delta_H(CCl_4)$ 1.2 (3 H, t), 1.5—2.0 (2 H, m), 2.1—2.2 (6 H, two singlets), 4.9—6.8 (4 H, m), and 7.2 (5 H, s); $\nu_{max.}$(film) 1 730, 1 240, and 970 cm^{-1}.

Oxidation of 5-*methyl*-1-*phenylhexa*-1,3-*diene* (**1f**). Treatment of the diene as described above gave two products. A mixture of 3-acetoxy-5-methyl-1-phenylhex-1-en-4-ol (**2f**) and 4-acetoxy-5-methyl-1-phenylhex-1-en-3-ol: $\delta_H(CCl_4)$ 0.9 (6 H, d), 1.2—2.1 (1 H, m), 2.0—2.1 (total 3 H, a pair of singlets), 2.3—3.1 (1 H, m), 4.0—5.1 (2 H, m), 5.8—6.7 (2 H, m), and 7.2 (5 H, s); $\nu_{max.}$(film) 3 450, 1 730, 1 245, and 975 cm^{-1}. 3,4-Diacetoxy-5-methyl-1-phenylhex-1-ene (**3f**): $\delta_H(CCl_4)$ 0.8—1.0 (6 H, d), 1.3—2.1 (1 H, m), 1.9—2.0 (total 6 H, a pair of singlets), 4.8—6.8 (4 H, m), and 7.2 (5 H, s).

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