

## Oxidation by Cobalt(III) Acetate. Part 3.<sup>1</sup> Allylic Oxidation of Various Olefins in Acetic Acid

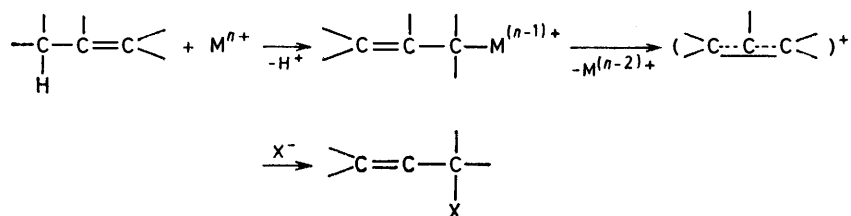
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Allylic oxidation of various olefins with cobalt(III) acetate in acetic acid under nitrogen has been investigated. The substrates studied include allylbenzene, oct-1- and -*trans*-4-ene, cycloalkenes (C<sub>5</sub>—C<sub>8</sub>), and 1- and 4-methylcyclohexene. The reaction gave exclusively the allylic acetate as the primary product; no 1,2-addition or skeletal rearrangement product was formed in significant amount. Some mechanistic aspects of allylic oxidation are discussed.

THERE is considerable interest in the allylic oxidation of olefins by various metal oxidants. The metal salts most thoroughly studied are Pb<sup>IV</sup>,<sup>2-5</sup> Hg<sup>II</sup>,<sup>2,6-8</sup> Tl<sup>III</sup>,<sup>4,9</sup> Pd<sup>II</sup>,<sup>10,11</sup> Se<sup>IV</sup>,<sup>12,13</sup> Cr<sup>VI</sup>,<sup>14,15</sup> Mn<sup>III</sup>,<sup>16</sup> *etc.*, and some similarities in their behaviour with olefins have been pointed out. For instance, the metal oxidant adds

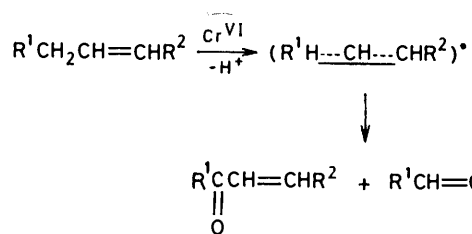
molysis of a metal oxidant acts as a chain-carrier, has also been proposed in some cases.<sup>4,5</sup>

Oxidation with cobalt(III) acetate has been extensively investigated and most of the results, on kinetic grounds,<sup>17-19</sup> have been successfully interpreted in terms of an electron-transfer mechanism including a radical



SCHEME 1 Oxymercuration-demercuration pathway for Pb<sup>IV</sup>, Hg<sup>II</sup>, Tl<sup>III</sup>, Pd<sup>II</sup>, and Se<sup>IV</sup>

electrophilically to the double bond in a Markovnikov manner, possibly through a  $\pi$ -complex, to form an organometallic adduct. Heterolytic cleavage of the adduct and subsequent addition of a nucleophile to the resulting



SCHEME 2 Direct hydrogen-abstraction pathway for Cr<sup>VI</sup>, Mn<sup>III</sup><sup>14</sup>

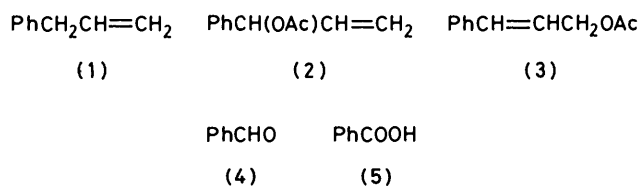
allylic cation afford the allylic product (Scheme 1). Although the detailed mechanism is still obscure, Se<sup>IV</sup> oxidation has been considered to proceed essentially *via* the mechanism shown in Scheme 1, and Guillemonat has proposed a general rule for the course of the reaction.<sup>12</sup>

Another mode of oxidation has been reported for Cr<sup>VI</sup> and Mn<sup>III</sup> in which a hydrogen atom (or hydride ion) is first abstracted from an allylic carbon to generate an allylic radical (or carbo-cation). The species so formed is further oxidized eventually to give the allylic product (Scheme 2).<sup>14</sup> Thirdly, an alternative hydrogen-abstraction mechanism, where a radical generated by the ther-

mal cation as an incipient intermediate. However, allylic oxidation with cobalt(III) acetate has been limited to cycloalkenes,<sup>17,20,21</sup> and it is apparent that the data are not adequate to specify the mechanism completely. Our previous study on the oxidation of  $\alpha$ - and *cis*- and *trans*- $\beta$ -methylstyrene with cobalt(III) acetate has demonstrated the competitive occurrence of 1,2-addition and allylic reactions.<sup>22</sup> This led us to investigate the allylic oxidation of various olefins having an active hydrogen at the allylic position. We now report some observations on these reactions with the oxidant in acetic acid.

### RESULTS

*Oxidation of Allylbenzene.*—Oxidation of allylbenzene (1) readily proceeded at 70 °C in acetic acid, giving four pro-



ducts, 1-phenylallyl acetate (2), cinnamyl acetate (3), benzaldehyde (4), and benzoic acid (5). No 1,2-addition product was formed. The product distributions are presented in Table 1.

TABLE 1

Product distribution from the oxidation of allylbenzene in acetic acid <sup>a</sup>

Experiment	t/h	Products (mol %)				
		(1) <sup>b</sup>	(2)	(3)	(4)	(5)
1	2	77	7.6	15		
2	5	60	10	23	0.9	2.9
3	10	54	11	27	1.1	5.0
4	24	44	10	35	2.4	7.8
5	30	38	4.6	36	4.1	9.1

<sup>a</sup> Under N<sub>2</sub>, at 70 °C; [Co(OAc)<sub>2</sub>]<sub>0</sub> 0.206M, [Allylbenzene]<sub>0</sub> 0.082M. <sup>b</sup> Recovered substrate in mole %.

The yield of products (3)—(5) increased as the reaction proceeded, while the allylic acetate (2) reached a maximum yield after *ca.* 10 h and then decreased after a longer reaction time. This can be ascribed to the thermal and cobalt-catalysed isomerization of (2) to (3). Control experiments showed that when (2) was heated in acetic acid at 60 °C for 20 h in the presence and absence of cobalt(III) acetate, (3) was obtained in 49 and 35% yield, respectively.<sup>22</sup> In the

TABLE 2

Oxidation of oct-1- and -*trans*-4-ene in acetic acid <sup>a</sup>

Experiment	Olefin	[Co <sup>III</sup> ] <sub>0</sub> / [Olefin] <sub>0</sub> mole	T/°C	[Olefin] <sup>b</sup>	Products (mole %)			
					(8)	(9)	(10)	(11)
6	(6)	2.5	60	71	3.8	4.0		
7		2.5	70	65	2.6	3.0		
8	(7)	5.0	60	21			37	5.1
9		2.5	70	47			32	2.8
10		5.0	70	21			35	4.6
11		2.5	80	34			31	4.0

<sup>a</sup> Under N<sub>2</sub> for 24 h, [Co(OAc)<sub>2</sub>]<sub>0</sub> 0.228M. <sup>b</sup> Recovered substrate in mole %.

former case, concomitant formation of the cleavage compounds (4) and (5) was observed.

*Oxidation of Aliphatic Olefins.*—The oxidation of aliphatic substrates was carried out under similar conditions to those above. No neutral product other than allylic acetate, identified by g.l.c., was formed in significant yield; hence product analyses were confined to estimating the allylic acetate. Likewise, no attempt was made to determine any

TABLE 3

Oxidation of cycloalkenes in acetic acid <sup>a</sup>

Experiment	Olefin	[Co <sup>III</sup> ] <sub>0</sub> / [Olefin] <sub>0</sub> mole	T/°C	[Olefin] <sup>c</sup>	3-Acetoxycycloalkenes <sup>b</sup>			
					(16)	(17)	(18)	(19)
12	(12)	2.5	40	*	31			
13		2.5	50	*	41			
14		2.5	60	*	41			
15	(13)	2.5	40	37			44	
16		5.0	50	12			49	
17		5.0	60	4.0			57	
18	(14)	2.5	40	67			26	
19		2.5	70	52			29	
20		5.0	70	32			41	
21	(15)	2.5	40	71				15
22		2.5	80	26				22
23		5.0	80	25				34

<sup>a</sup> Under N<sub>2</sub> for 24 h, [Co(OAc)<sub>2</sub>]<sub>0</sub> 0.228M. <sup>b</sup> Products in mole %. <sup>c</sup> Recovered substrate in mole %.

\* Exact values are unknown because of loss of (12) during work-up and/or analytical procedure attributable to its volatility.

acidic products formed. The results are presented in Tables 2—4.

*Oxidation of Oct-1- and -trans-4-ene.*—At 60—70 °C for 24 h, the oxidation of oct-1-ene (6) gave 3-acetoxyoct-1-ene (8) and 1-acetoxyoct-2-ene (9) in 3—4% yield, and *trans*-oct-4-ene (7) afforded 3-acetoxyoct-4-ene (10) as a main

TABLE 4

Oxidation of methyl-substituted cyclohexenes in acetic acid <sup>a</sup>

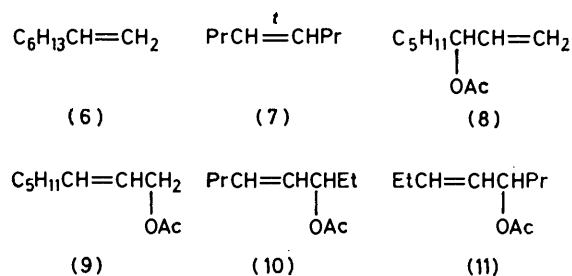
Experiment	Olefin	[Co <sup>III</sup> ] <sub>0</sub> / [Olefin] <sub>0</sub> mole	T/°C	[Olefin] <sup>b</sup>	Products (mole %)		
					(22)	(23)	(24)
24	(20)	2.5	40	18	28	1.0	
25		5.0	40		59	1.0	
26		2.5	50	5.6	37	4.0	
27		5.0	50		42	6.0	
28	(21)	2.5	50	27		46	
29		5.0	50	1.0		59	

<sup>a</sup> Under N<sub>2</sub> for 24 h, [Co(OAc)<sub>2</sub>]<sub>0</sub> 0.228M. <sup>b</sup> Recovered substrate in mole %.

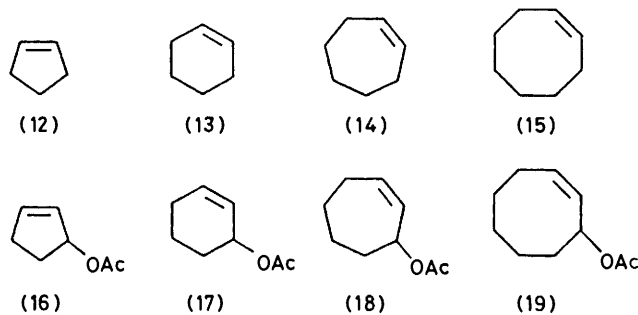
product, along with a minor amount of 5-acetoxyoct-3-ene (11).

The surprisingly small yield of oxidation products in the case of oct-1-ene remains unexplained; perhaps, there are competing unproductive side-reactions as yet not elucidated.

*Oxidation of Cycloalkenes.*—Although the reactions were slow compared with those observed for the reactions in the



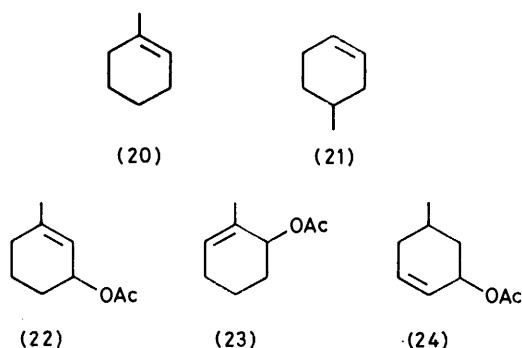
presence of trifluoroacetic acid (TFA),<sup>21</sup> the oxidation of cycloalkenes (12)—(15) in acetic acid gave corresponding 3-acetoxycycloalkenes (16)—(19), respectively. The reactivities of (14) and (15) towards Co<sup>III</sup> were low compared with those of (12) and (13), but an appreciable increase in the yields of the allylic acetates was observed at elevated tem-



perature and in the presence of high concentration of cobalt(III) acetate.

*Oxidation of 1- and 4-Methylcyclohexene.*—Both 1- (20) and 4-methylcyclohexene (21) were found to be oxidized more readily than cyclohexene under comparable conditions. It is noteworthy that the reactions give the products in

surprising high selectivities at the competing sites on the same cyclohexane ring; 1-methylcyclohexene gave 3-acetoxy-1-methylcyclohexene (22) as the main product, along with only a minor amount of 6-acetoxy-1-methyl-



cyclohexene (23) and, in the case of (21), solely 3-acetoxy-5-methylcyclohexene (24) was obtained.

#### DISCUSSION

Allylic oxidation of olefins with cobalt(III) acetate was found to proceed under mild conditions, giving the allylic acetate in moderate yield. Optimum conditions have not been evaluated, but the use of a high concentration of cobalt(III) acetate results in an increased yield of the allylic acetate.

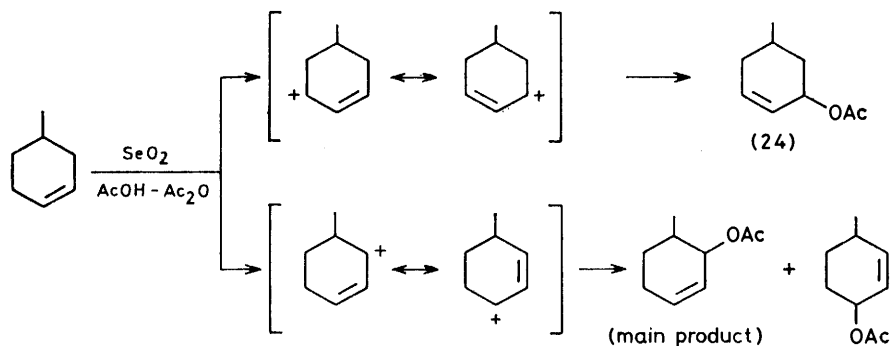
Another pronounced feature of the present reaction is the steric control of attack by  $\text{Co}^{\text{III}}$  at a hindered site. Unlike  $\text{Pb}^{\text{IV}}$  and  $\text{Hg}^{\text{II}}$  oxidations,<sup>2</sup> in which (23) was obtained from (20), the 3-acetoxyated compound (22) was obtained with cobalt(III) acetate as the major product. In the case of 4-methylcyclohexene, oxidation by selenium dioxide in acetic acid containing acetic

Although detailed information on the intermediate is not provided by the reactions so far studied, we observe a close relationship between the present reactions and previous reports. Verstraelen and his co-workers examined the oxidation of cycloalkenes ( $\text{C}_5$ – $\text{C}_8$ ) with cobalt(III) acetate in  $\text{AcOH}$ – $\text{TFA}$ , yielding 3-acetoxy-cycloalkenes as a sole or major product.<sup>21</sup> They tentatively proposed a cobalt-co-ordinated intermediate to explain the observed reactivity order of cycloalkenes towards  $\text{Co}^{\text{III}}$ . Although the rates were low in acetic acid, the order of reactivities of the cycloalkenes in the present reactions were essentially the same as that observed in the  $\text{TFA}$ -catalysed reaction, *viz.*  $\text{C}_5 < \text{C}_6 > \text{C}_7 > \text{C}_8$ . This mechanism is also consistent with our failure to detect any phenyl-rearrangement product in the oxidations of styrene<sup>1</sup> and  $\alpha$ -methylstyrene<sup>22</sup> with cobalt(III) acetate. For these unsymmetrical olefins, skeletal rearrangement is generally accepted and the phenomenon should be ascribed to the formation of an open carbocation resulting from carbon–metal heterolytic cleavage as typically observed in  $\text{Pb}^{\text{IV}}$  oxidations.<sup>26,27</sup>

Considerations of the relative stability of possible intermediates and the steric and electronic aspects of the subsequent addition of a nucleophile are beyond the scope of this report. The products and selectivities must be determined by the combination of several factors, whose elucidation would provide a more satisfactory explanation of the results.

#### EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were measured for solutions in  $\text{CCl}_4$  or  $\text{CDCl}_3$  on a JEOL model JNM-C-HL spectrometer. I.r. spectra were determined for liquid films on a JASCO DS-403G spectrophotometer. G.l.c. was carried out on a



SCHEME 3

anhydride gave a mixture of three allylic acetates (Scheme 3).<sup>12</sup> On the other hand, (21) gives the sole product (24). These results suggest the intervention by steric hindrance of the methyl group which limits the attack of  $\text{Co}^{\text{III}}$  at a hindered site, since the position  $\alpha$  to the methyl group was completely or largely insensitive to  $\text{Co}^{\text{III}}$ . As is often the case with branched alkanes,<sup>23</sup> this steric factor can be explained in terms of the bulkiness of cobalt(III) acetate, which is a dimeric species in acetic acid.<sup>24,25</sup>

Shimadzu GC-6A instrument, with a 2-m column packed with 5% PEG-20M on Chromosorb G. For the measurement of yields, biphenyl was used as internal standard. Preparative g.l.c. was performed on a Shimadzu GC-4A instrument, with a 2-m column packed with 30% PEG-20M on Celite 545, attached to a Shimadzu APP-5 fraction collector through a glass joint. Mass spectra were determined on a Shimadzu GC-MS 7000 spectrometer which was coupled *via* a heated column to the g.l.c. apparatus.

*Starting Materials.*—Olefins other than 1-methylcyclohexene were commercial materials and were purified by

distillation just before use. 1-Methylcyclohexene was prepared by a known method.<sup>28</sup> Purities were checked by g.l.c. analysis. Cobalt(III) acetate was obtained by oxidation of cobalt(II) acetate tetrahydrate in acetic acid containing acetic anhydride,<sup>25</sup> and the conversion into Co<sup>II</sup> was determined by addition of an excess of Fe<sup>II</sup> and back-titration of the residual Fe<sup>II</sup> ion with Ce<sup>IV</sup>.

**Oxidation Procedure.**—A typical oxidation procedure was as follows. Allylbenzene and biphenyl (internal standard) in acetic acid were mixed with a solution of cobalt(III) acetate in acetic acid in a reaction vessel (ca. 10 ml). The vessel was then flushed with dry nitrogen gas, sealed with a silicone-rubber stopper, and maintained at a controlled temperature in a thermostat without agitation. At the end of the experiment, the reaction solution was poured into water and the products were extracted with ether. The extract was successively washed with aqueous sodium carbonate and water and then dried (Na<sub>2</sub>SO<sub>4</sub>). Evaporation left a brown oil which was analysed by g.l.c. To determine the acidic product, the aqueous layer was acidified with hydrochloric acid to liberate the acid which was again extracted with ether. The extract was evaporated and the residue was recrystallized from water to give benzoic acid, m.p. 121 °C.

**Identification of Products.**—Reaction products other than benzoic acid were identified from their g.l.c. retention times. 3-Acetoxy-cyclo-heptene (18) and -octene (19) and 3-acetoxy-oct-4-ene (10) were also isolated by preparative g.l.c. and were identified by n.m.r., i.r. and mass spectra. Compounds obtained from Ru-catalysed hydrogenation of 3-acetoxy-1-methylcyclohexene (22) and 3-acetoxy-5-methylcyclohexene (24) were identified as a common product, 3-acetoxy-1-methylcyclohexane.

**Reference Compounds.**—Benzaldehyde was commercial material.  $\alpha$ -Phenylallyl acetate was prepared by the reaction of phenylmagnesium bromide with acrolein and subsequent acetylation of the resultant alcohol. Cinnamyl acetate was obtained by acetylation of the corresponding alcohol with acetic anhydride. 3-Acetoxy-cyclo-pentene (16) and -hexene (17) were prepared by Gilmore's method,<sup>16</sup> 3-Acetoxyoct-1-ene (8) was prepared according to the literature.<sup>4</sup>

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[0/891 Received, 10th June, 1980]