Oxidation by Cobalt(III) Acetate. Part 6.[1] A Novel Synthesis of the Glycol Monoacetates from Aromatic Olefins in Wet Acetic Acid

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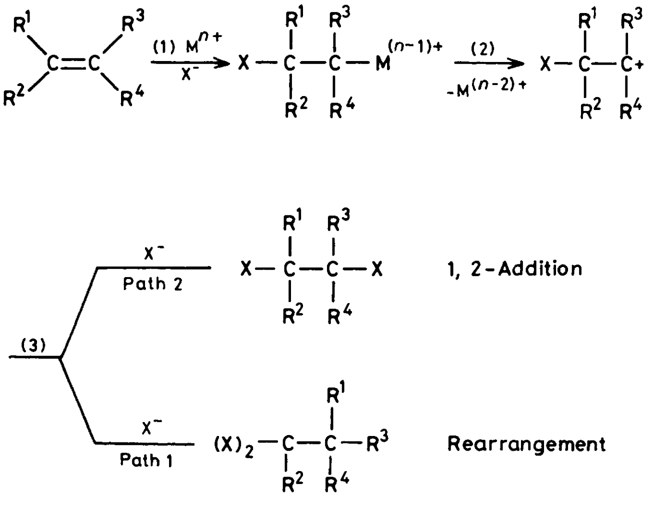
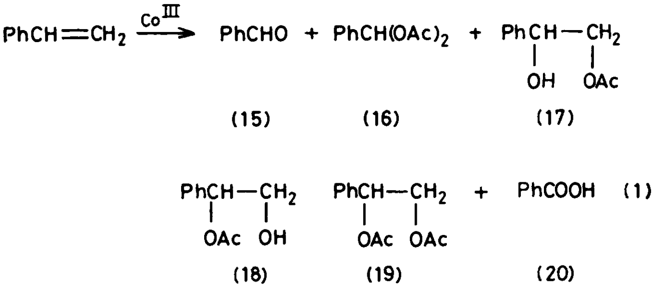
Oxidation of various aryl-conjugated olefins with cobalt(III) acetate in wet acetic acid under nitrogen affords the glycol monoacetates in moderate to good yields. None of the phenyl rearrangement product is formed in the present reactions. These results are best interpreted by assuming the formation of a Co-co-ordinated intermediate.

Oxidation of olefins with metal oxidants has been extensively studied.[2-8] The mechanism is well established and consists, in summary, of (1) electrophilic addition of an oxidant to olefin to form an organometallic adduct, (2) heterolytic metal–carbon cleavage to generate an open carbocation, which is stabilized as a cyclic 'onium ion by neighbouring group participation, and (3) addition of a nucleophile to the resulting ion. A pronounced feature of the reaction with the oxidants is the tendency of the initially formed carbocation to rearrange, especially if, in doing so, a potentially more stable ion results (path 1 in Scheme 1). One striking example is the rearrangement of the phenyl group in an unsymmetrical aromatic olefin *via* an intermediate phenonium ion; the migratory aptitude of the group could be related to the ability of the substituent on the benzene ring to stabilize the ion, *i.e.* electron-donating property, *viz.* p-MeO > p-Me > p-H > p-Cl, p-Br.[9] Thus, the relative significance of the two paths strongly depends on the structure of the olefin and nature of the oxidant as well as the reaction conditions employed, resulting in the formation of a complex mixture of 1,1- and 1,2-adducts. Consequently, it is comparatively rare that a sole product is obtained in a synthetically useful yield.

On the basis of the kinetic results, oxidation with cobalt(III) acetate has been considered to occur *via* an electron-transfer mechanism.[10-12] In a limited number of cases, a radical cation has been detected by e.s.r. spectroscopy.[13,14] However, only a few studies have been made on the oxidation of olefins with cobalt(III).[15,16] In recent studies, we observed the predominant formation of the glycol monoacetates in the oxidation of styrene[17] and α-methylstyrene[18] with cobalt(III) acetate in acetic acid. This led us to investigate the reaction of various aryl-conjugated olefins with the oxidant. In the present paper, we report a simple and novel method for preparing glycol monoacetates and discuss some mechanistic aspects of the reactions.



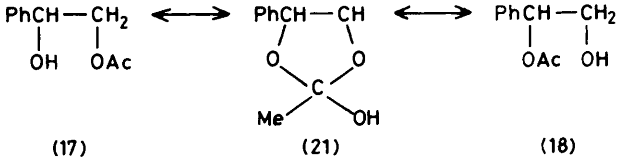
Scheme 1. M = Pb (n = 4), Tl (n = 3), Hg (n = 2), *etc.*, X = solvent or additive



$$\mathrm{PhCH{=}CH_2} \xrightarrow{\mathrm{Co^{III}}} \underset{(15)}{\mathrm{PhCHO}} + \underset{(16)}{\mathrm{PhCH(OAc)_2}} + \underset{(17)}{\mathrm{PhCH(OH){-}CH_2OAc}} + \underset{(18)}{\mathrm{PhCH(OAc){-}CH_2OH}} + \underset{(19)}{\mathrm{PhCH(OAc){-}CH_2OAc}} + \underset{(20)}{\mathrm{PhCOOH}} \quad (1)$$

Results and Discussion

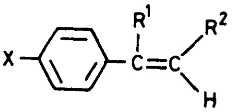
Styrene was readily oxidized with cobalt(III) acetate at 60 °C in acetic acid under nitrogen, giving a mixture of carbon–carbon cleavage compounds (15) and (16), 1,2-adducts (17)—(19), and benzoic acid (20) [equation (1)]. The main products, the glycol monoacetates (17) and (18), are known to be interconvertible *via* the intermediate (21) even at room temperature[19] and because of this we could not establish their exact product ratio by the present technique. The glycol monoacetates appeared as one peak on g.l.c. analysis, so that these were estimated as a single group.



It should be noted that addition of small amounts of water to the system resulted in increased yield of the glycol monoacetates. Thus the glycol monoacetates were obtained in 83% yield at 95% conversion of styrene under the conditions in Table 1. The yields of the other products decreased on addition of water and there were no significant new products; at this time, (15), (16), (19), and (20) were obtained in 1.6, 1.9, 4.2, and 5.6 mole%, respectively. It seems therefore that water not only contributes to the formation of the glycol monoacetate, but also inhibits any side-reactions.

Oxidation of the other olefins was carried out in wet acetic acid in a manner similar to that of styrene, resulting in

Table 1. Formation of the glycol monoacetates form Co^{III} oxidation of various aromatic olefins in wet acetic acid [a]



	R^1	R^2	X	Temperature (°C)	Time (h)	Recovered olefin (%)	Glycol monoacetates (%) [b]
(1)	H	H	H	60	24	5.2	83
(2)	H	H	Me	70	15	0.7	84
(3)	H	H	Cl	70	20	7.0	83
(4)	H	H	Br	70	20	7.2	72
(5)	H	H	MeO [c]	40	2		22
(6)	H	H	NO_2	70	24	31	51
(7)	Me	H	H	60	20	0.6	80
(8)	Me	H	Me	50	20	7.7	75
(9)	H	Me	H [d,*]	60	20	39	7.3
(10)	H	Me	H [d,†]	60	20	14	15
(11)	H	Me	MeO	Ambient	2		75
(12)	Ph	H	H	70	24	31	72
(13)	H	Ph	H [c,*]	70	24	15	53
(14)	H	Ph	H [c,†]	70	15	11	54

[a] Under N_2, $[Co(OAc)_3]_0$ 0.2657M; $[Co^{III}]_0/[Olefin]_0$ 2.5; $[H_2O]_0/[Co^{III}]_0$ 8.0 (mole ratio). [b] G.l.c. yields based on the substrates consumed. [c] $[Co^{III}]_0/[Olefin]_0$ 2.0 (mole ratio). [d] Main products of these reactions were the allylic acetates and explanation of the results has been reported.[18]

* *cis*. † *trans*.

Table 2. Formation of oxidative rearrangement products [a]

Olefins	Rearrangement products		Oxidants		
			Co^{III}	Tl^{III} [b]	Pb^{IV}
(1)	$PhCH_2CH(OAc)_2$	(22)	*	7.6	47 [c]
(3)	*p*-$ClC_6H_4CH_2CH(OAc)_2$	(23)	*	5.8	30 †,[c]
(5)	*p*-$MeOC_6H_4CH_2CH(OAc)_2$	(24)	*	64	94†,[d]
(7)	$PhCH_2COMe$	(25)	1 [e]		46 [f]
	PhCH(OAc)COMe	(26)	2 [e]		4.2 [f]

[a] G.l.c. yield (%). [b] Ref. 6. [c] Ref. 2. [d] Ref. 4. [e] Ref. 18. [f] Ref. 3.

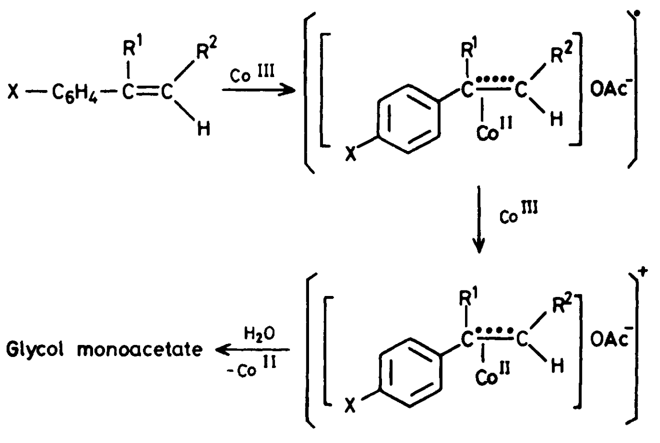
* Not detected. † Isolated yield.

predominant formation of corresponding glycol monoacetates (Table 1). In the cases of (9) and (13), rearrangement of *cis*-olefin to the *trans*-isomer was observed. The reaction conditions (concentration of the oxidant, temperature, and time) were determined on the basis of reactivities of the substrates as well as susceptibilities of the glycol monoacetates towards further oxidation and/or acetylation. No neutral product other than glycol monoacetate and a minor amount of 1,2-diacetate, identified by g.l.c., was formed in significant yield. Hence product analyses were confined to estimating the glycol monoacetates, except for a few compounds involving phenyl rearrangement (see also Table 2). Likewise no attempt was made to determine any acidic products formed.

Compared with the other *p*-substituted styrenes, oxidation of (6) which has a strong electron-withdrawing nitro-group did not proceed readily. Indeed, 31% of the olefin was recovered even after 24 h at 70 °C. On the other hand, *p*-MeO-substituted olefins (5) and (11) showed exceptionally high reactivities, and the substrates were completely consumed within 2 h at lower temperature.

Another remarkable feature of the present reaction is that there is no formation of the phenyl rearrangement product. Comparisons of the results obtained from the present work for a few olefins with published data are presented in Table 2. Unlike Pb^{IV} and Tl^{III} oxidations, the present results provide no evidence for the formation of the rearrangement product in the reactions of (1), (3), and (5). There was no extensive formation of rearrangement products in the oxidation of α-methylstyrene, although the olefin is expected to be a highly rearrangement-prone compound. It should be noted, therefore, that the electronic properties of the *para*-substituted styrenes (1)—(7) affected mainly the reactivity of the olefins, but scarcely the distribution of the products. An unexpectedly low yield of the product in the case of *p*-methoxystyrene remained unexplained; perhaps there might be competing unproductive side-reactions as yet not elucidated.

Mechanism.—The oxidation of various aryl-conjugated olefins with cobalt(III) acetate in wet acetic acid leads exclusively to the formation of the glycol monoacetates, along with minor amounts of the 1,2-diacetates. The formation of 1,2-adducts is considered to occur by addition of nucleophiles to a cationic intermediate. In the present reaction the cationic intermediate would be expected to react with the most accessible nucleophile, AcOH, giving the 1,2-diacetate. However, the results clearly show the predominant incorporation of a hydroxy- rather than an acetoxy-group. By analogy with alternative processes such as the wet Prevost reaction and Pb^{IV} oxidation, it appears that glycol monoacetate results from the reaction of adventitious water with the acetoxonium ion. The participation of the acetoxy-group, however, is



Scheme 2.

inconsistent with the present observations that (1) the yield of the 1,2-diacetate is too low compared with that of the glycol monoacetate, and (2) there is no extensive formation of phenyl rearrangement product in the oxidation of unsymmetrical olefins. In addition, we also observed that added acetate ion had little effect on the yield of the 1,2-adducts in the oxidation of styrene.[17] Consequently, it is likely that oxidation with cobalt(III) proceeds by a different mechanism from that observed in the reactions with other oxidants. Even if the present reaction proceeds *via* a stepwise mechanism such as shown in Scheme 1, a lack of the rearrangement product indicates no formation of an open carbocation resulting from metal–carbon cleavage. Hence, for the present reaction we propose a mechanism proceeding *via* an electron-transfer step (Scheme 2) in which Co^{III} co-ordinates with the olefin to form a Co-co-ordinated intermediate. The lack of oxidative rearrangement of the phenyl group can be adequately explained by conversion of the Co-co-ordinated radical into a cation and subsequent addition of water to the latter and/or insertion of the cobalt hydroxy-ligand * to yield the glycol monoacetate. There is evidence that the phenyl group contributes towards a stabilization of the intermediate, and an explanation for this has been reported.[18] In this way the intermediate is considered to be stabilized by conjugation extended over the aromatic ring without formation of a cyclic 'onium ion such as acetoxonium or phenonium, with the participation of the neighbouring acetoxy or phenyl group, respectively. Accordingly, the apparent order of reactivity of *para*-substituted styrenes can be related to the relative stability of the intermediate.

In summary, the oxidation of styrenes and some related olefins with cobalt(III) acetate in wet acetic acid affords glycol monoacetates in moderate to good yields. There are limitations on the synthetic utility for some olefins, but the present method is as useful for the preparation of the glycol monoacetates as alternative processes such as acetolysis of epoxides,[19] reaction of AgOAc with I_2 and olefins (wet Prevost reaction) or with 1,2-dibromides [22,23] in wet acetic acid, electrolytic acetoxylation–hydroxylation of olefins,[24] and so on.

Although detailed information on the possible intermediates and initial interaction of Co^{III} with olefins is not fully provided by the reactions so far studied, further consideration of steric and electronic aspects of the reaction should offer a more satisfactory explanation of the results.

Experimental

^1H N.m.r. spectra were measured for solutions in CCl_4 or $CDCl_3$ on a JEOL model JNM-C-HL spectrometer. I.r. spectra were determined on a JASCO DS-403G spectrophotometer. G.l.c. was carried out on a Shimadzu GC-4CM instrument, with a 2 m column packed with 1.5% Silicone OV-17 on Shimalite W. 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. M.p.s were measured on a Yamato capillary m.p. apparatus.

Starting Materials.—Cobalt(III) acetate was prepared either by peracetic acid oxidation [20] or ozonization [21] of cobalt(II) acetate tetrahydrate in acetic acid containing acetic anhydride. The conversion into Co^{III} as determined by Fe^{II} and back-titration with Ce^{IV} as well as determination of total cobalt by EDTA titration was $> 95\%$. Olefins (1), (7), and (9)—(14) were commercial materials, and (2), (3), (4), and (8) were prepared by dehydration of the corresponding α-phenethyl alcohol with $KHSO_4$.[25] Other substrates (5) [26] and (6) [27] were obtained according to the literature. All the olefins were purified by distillation or recrystallization just before use and their purity was checked by g.l.c. analysis.

Oxidation Procedures.—The following oxidation procedure is representative. Styrene (2.21 g, 21.3 mmol) was mixed with 2.5 mol. equiv. (53.1 mmol) of cobalt(III) acetate in acetic acid (200 ml) and water (7.65 g, 425 mmol) in a reaction vessel. The vessel was then flushed with dry nitrogen gas, sealed with a glass stopper, and maintained at a controlled temperature (60 °C) in a thermostat without agitation. After 24 h, the mixture was poured into water and the product was extracted three times with ether. The extracts were successively washed with aqueous sodium carbonate and water and then dried ($MgSO_4$). Evaporation of the solvent left an oil which was analysed by g.l.c.

All the glycol monoacetates were identified from their g.l.c. retention times as well as mass spectrometry, and their g.l.c. yields were obtained by adding an internal standard such as biphenyl.

Reference Compounds.—The glycol monoacetates except the following four were prepared by AgOAc–I_2 reaction in wet acetic acid (wet Prevost reaction), and after work-up procedures the products were chromatographed on silica gel (hexane–AcOEt).

The monoacetates of 1,1-[24] and 1,2-diphenylethane-1,2-diol [23] were obtained by conventional procedures and were purified by recrystallization from benzene–hexane. The monoacetates of 1-(*p*-methoxyphenyl)-ethane- and -propane-1,2-diol were isolated from oxidation mixtures of the corresponding olefins with cobalt(III) acetate in wet acetic acid by preparative t.l.c. on silica gel (hexane–AcOEt) and were identified by i.r. and n.m.r.

Other reference compounds (22),[2] (23),[2] (24),[4] (25),[28] and (26) [3] were obtained by known methods.

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* Cobalt(III) acetate is considered as a di-μ-hydroxybinuclear complex; [20,21] concerning the formation of the glycol monoacetate, see also refs. 16 and 17.

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