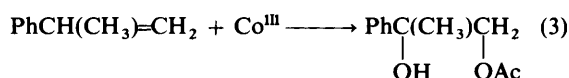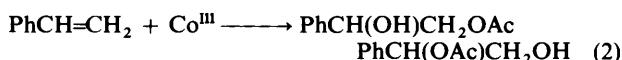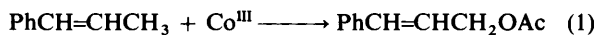# Oxidation by Cobalt(III) Acetate. Part 8.[1] Effects of Substituents on Product Distributions in Oxidation of Aromatic Olefins by Cobalt(III) Acetate

Takashi Morimoto,* Masao Hirano, and Tsuyoshi Koyama
Department of Industrial Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

Oxidation of aromatic olefins by cobalt(III) acetate in acetic acid under nitrogen gave both allylic acetates and glycol monoacetates. Disubstituted olefins were oxidized by the oxidant to give predominantly allylic acetates. Glycol monoacetates were minor products except for the case of 1-phenylisobutene which was slowly oxidized to give the corresponding glycol monoacetate. In the oxidation of tri- and tetra-substituted olefins, the yield of glycol monoacetate increased at the expense of that of allylic acetate. A mechanism, in which the reaction proceeds through a Co-co-ordinated radical cation formed by an one-electron abstraction from olefin by cobalt(III) acetate, is suggested.

Oxidation of olefins by cobalt(III) acetate in acetic acid proceeds *via* the dual mechanism of 1,2-addition reaction across the double bond [2–4] and allylic oxidation. [1,5,6] When the olefin has active hydrogens at an allylic site, allylic acetate is obtained predominantly. On the other hand, when it has no allylic hydrogen, 1,2-addition reactions occur [equations (1) and (2)]. However, oxidation of α-methylstyrene by cobalt(III) acetate gives exclusively the 1,2-addition product, glycol monoacetate, although it has allylic hydrogens [equation (3)]. Furthermore, we have already reported that 1-methylcyclohexene was oxidized by the oxidant to give selectively the corresponding allylic acetate, but we found in this study that oxidation of 1-phenylcyclohexene afforded glycol monoacetates as the main product.

$$PhCH{=}CHCH_3 + Co^{III} \longrightarrow PhCH{=}CHCH_2OAc \quad (1)$$

$$PhCH{=}CH_2 + Co^{III} \longrightarrow PhCH(OH)CH_2OAc$$
$$PhCH(OAc)CH_2OH \quad (2)$$

$$PhCH(CH_3){=}CH_2 + Co^{III} \longrightarrow Ph\underset{\underset{OH}{|}}{C}(CH_3)\underset{\underset{OAc}{|}}{C}H_2 \quad (3)$$

These results seem to show that for cobalt(III) acetate oxidation of aromatic olefins, the product distribution is influenced by the number of substituents on the double bond in addition to whether it has allylic hydrogens or not. The change of products or their distribution sometimes points out the intermediates involved in the reaction and clarifies the mechanism.[7]

In this paper, we report the effects of substituents attached to double bonds on the products and their distribution in the oxidation of various aromatic olefins by cobalt(III) acetate in acetic acid under nitrogen and also suggest a mechanism.

Results

Oxidation of 1-Phenylcyclohexene (1).—Oxidation of (1) by cobalt(III) acetate in acetic acid under nitrogen gave a mixture of 2-acetoxy-1-phenylcyclohexanol (2) and 2-acetoxy-2-phenyl-cyclohexanol (3) with minor amounts of 3-acetoxy-1-phenyl-cyclohexene (4), 6-acetoxy-1-phenylcyclohexene (5), and biphenyl (6). These results are summarized in Table 1.

(1)

Co^{III}, AcOH

(2)   (3)   (4)   (5)   (6)
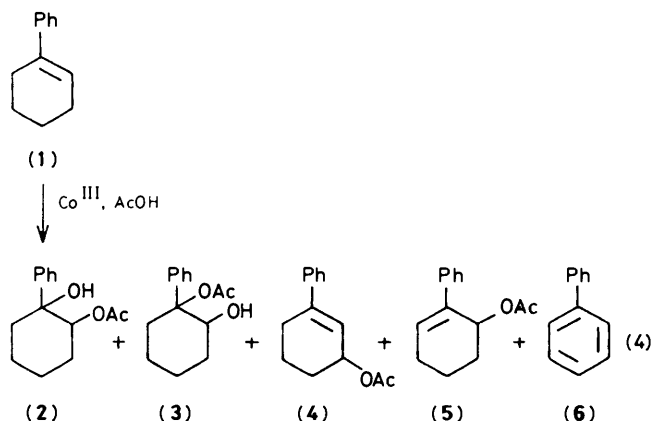
A change in the reaction conditions did not show any serious change in the product distribution.

Oxidation of 1-Phenylprop-1-ene Derivatives (7).—It has already been reported[6] that 1-phenylprop-1-ene (7a) was oxidized by cobalt(III) acetate in acetic acid to give exclusively allylic oxidation product, 3-acetoxy-1-phenylprop-1-ene (8a), and diol derivative (9a) was hardly formed.

The reaction of (*E*)-2-phenylbut-2-ene (7b) with cobalt(III)

Table 1. Oxidation of 1-phenylcyclohexene (1) by cobalt(III) acetate in acetic acid. [Co^{III}]$_0$ 0.0811M

[Olefins]$_0$/[Co^{III}]$_0$ Mole ratio	Temp. (°C)	Time (h)	Recovered olefin (mole %)	Product (mole %)			
				(2) + (3)	(4)	(5)	(6)
1	60	3	49.4	36.0	10.0	0.9	0.5
2	60	8	5.5	56.9	12.1	2.0	0.9
2.5	70	3	0	50.5	13.1	1.6	2.1
5.0[a]	40	24	0	1[b]	59.0[c]	1[d]	

[a] Oxidation of 1-methylcyclohexene. See ref. 6. [b] A mixture of 2-acetoxy-1-phenyl- and 2-acetoxy-2-phenyl-cyclohexanol. [c] 3-Acetoxy-1-methylcyclohexene. [d] 6-Acetoxy-1-methylcyclohexene.

Table 2. Oxidation of 1-phenylpropene derivatives (7)[a] by cobalt(III) acetate in acetic acid

[Olefin]$_0$/M	[Co^{III}]$_0$/M	Temp. (°C)	Time (h)	Recovered olefin (mole %)	Products (mole %)			
					(8)	(9)	(10)	PhCOR
R = H[b]								
0.116	0.291	60	20	14	52	13		8
R = CH$_3$								
0.050	0.102	40	15	24	12	53	1	6
0.050	0.102	60	15	3	12	69	4	10
R = Ph								
0.073	0.146	60	16	11	53	38		5
0.074	0.140	60	24	10	47	19		11

[a] PhC(R)=CHCH$_3$. [b] Data from ref. 3.

Table 3. Oxidation of 1-phenylbut-1-ene derivatives (11)[a] by cobalt(III) acetate in acetic acid

[Olefin]$_0$/M	[Co^{III}]$_0$/M	Temp. (°C)	Time (h)	Recovered olefin (mole %)	Products (mole %)				
					(12)	(13)	(14)	(15)	PhCOR
R = H									
0.0358	0.0705	40	16	29	36	6.0			5.1
0.0235	0.0705	60	16	3	58	4.1			
R = CH$_3$									
0.0460	0.0920	60	14	23	17	32	2.4		9.7
0.0460	0.0920	80	14	5	1.5	35	7.3		22
R = Ph									
0.145	0.289	60	8	6	2.9	65		10	8.1
0.145	0.289	80	8	2	2.3	46		40	10

[a] PhC(R)=CHCH$_2$CH$_3$.

acetate under similar conditions was found to give 3-acetoxy-2-phenylbutan-2-ol (9b) as the main product, and 1-acetoxy-3-phenylbut-2-ene (8b) and 1-acetoxy-2-phenylbut-2-ene (10) were minor products. Acetophenone was also detected in the product mixture. This distribution is much different from that in the oxidation of (7a). Although the reaction conditions were changed, there was no serious difference in the product distributions. The effects of added water and acetic anhydride on the product distributions were also examined since their addition markedly increased the yield of glycol monoacetate in

Ph—C=CHCH$_3$

R

(7)

AcOH Co^{III}

Ph—C=CHCH$_2$OAc   +   Ph—C—CHCH$_3$ (5)

R   OH OAc

(8)   (9)

Ph—C = CHCH$_3$

CH$_2$OAc

a: R = H
b: R = CH$_3$
c: R = Ph

(10)

the oxidation of various styrenes.[2,3] However, the addition did not produce any serious change in the product distributions. This effect were examined for all substrates used in the present study and the same results were obtained. Table 2 lists the results of oxidation of (7a—c).

Oxidation of 1,1-diphenylpropene (7c) by the oxidant afforded both 2-acetoxy-1,1-diphenylpropan-1-ol (9c) and 3-acetoxy-1,1-diphenylpropene (8c) with slightly more of (9c) than of (8c). Further oxidation products were also detected.

Oxidation of 1-Phenylbut-1-ene Derivatives (11).—Oxidation of 1-phenylbut-1-ene derivatives with cobalt(III) acetate in acetic acid under nitrogen was carried out in order to compare the results with those for (7). The results obtained are summarized in Table 3. Oxidation of 1-phenylbut-1-ene (11a) by cobalt(III) acetate gave exclusively 3-acetoxy-1-phenylbut-1-ene (12a) together with less than 10 mole % of a mixture of 2-acetoxy-1-phenylbutan-1-ol and 1-acetoxy-1-phenylbutan-2-ol (13a) and a small amount of benzaldehyde. These results are very close to those of oxidation of (7a). Benzoic acid was formed in oxidations of (11a), (16a), and (20a), but it was neglected in almost all runs because of its low yield.

2-Phenylpent-2-ene (11b) was oxidized by the oxidant under similar conditions to give a mixture of 4-acetoxy-2-phenylpent-2-ene (12b) and 3-acetoxy-2-phenylpentan-2-ol (13b) together with a small amount of 1-acetoxy-2-phenylpent-2-ene (14). Compound (13b) was formed in greater amount than (12b), showing the same tendency as those in oxidation of (7b) except that allylic acetate (12b) was formed in considerable amount.
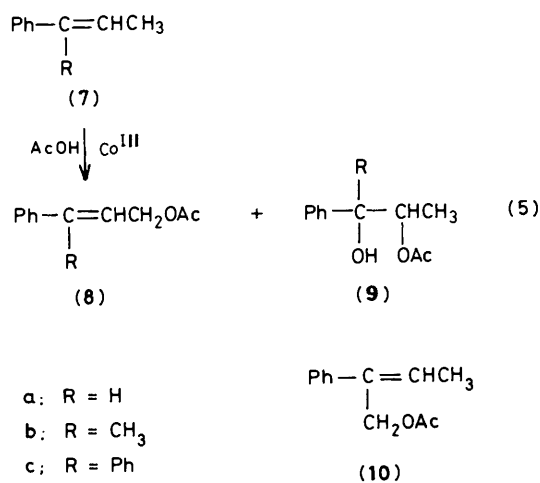
Table 4. Oxidation of 1-phenyl-3-methylbut-1-ene derivatives (16)[a] by cobalt(III) acetate in acetic acid

		Temp. (°C)	Time (h)	Recovered olefin (mole %)	Products (mole %)	
[Olefin]$_0$/M	[Co^{III}]$_0$/M				(17)	PhCOR
R = H						
0.0406	0.0812	60	4	72	9.4	5.8
0.0276	0.0812	60	4	62	13	4.6
R = CH$_3$						
0.0302	0.0604	60	2	38	39	8.1[b]
0.0302	0.0604	60	4	30	41	12[b]
R = Ph						
0.118	0.235	60	3	54	42	
0.0407	0.235	60	3	23	67	

[a] PhC(R)=CHCH(CH$_3$)$_2$. [b] PhC(CH$_2$OAc)=CHCH(CH$_3$)$_2$ (19) was also obtained (ca. 3—4% yield).

That the yield of (12b) was more than that of (8b) is, perhaps, due to the higher reactivity of the allylic hydrogen in (11b) than those in (7b) since a methylene group is generally more reactive than a methyl group.
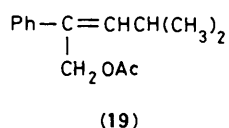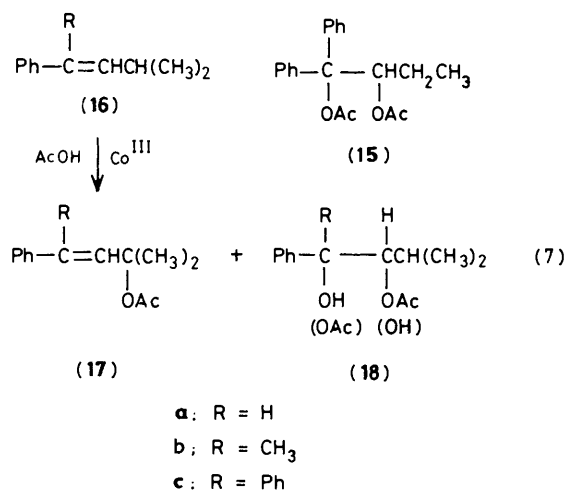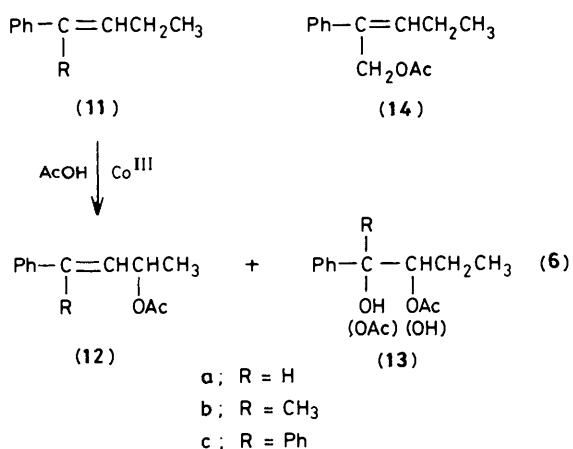
Oxidation of 1,1-diphenylbut-1-ene (11c) by the oxidant under same conditions led to formation of 2-acetoxy-1,1-diphenylbutan-1-ol (13c) and its acetate (15), and 3-acetoxy-1,1-diphenylbut-1-ene (12c) which was formed in small amount. The yield of diacetate (15) increased with temperature, showing that the compound resulted from the acetylation of (13c) and not from the direct reaction of olefin and the oxidant.

Oxidation of 3-Methyl-1-phenylbut-1-ene Derivatives (16).— Aromatic olefins which had tertiary allylic hydrogens were oxidized by cobalt(III) acetate in acetic acid under nitrogen in connection with the oxidation of olefins with primary and secondary allylic hydrogens. The results are summarized in Table 4.

The reaction of (16a) with cobalt(III) acetate was slower than those of disubstituted olefins which had primary and secondary allylic hydrogen, (7a) and (11a), and the glycol monoacetate was obtained in low yield together with a trace of benzaldehyde. No allylic acetate was obtained, although allylic oxidation was favourable in oxidations of (7a) and (11a).

When R was replaced by a methyl group, the reaction was accelerated and the corresponding glycol monoacetate (18b) was obtained as the main product with a small amount of 1-acetoxy-4-methyl-2-phenylpent-2-ene (19). No (17b) was detected in the reaction mixture by g.l.c. analysis. It should be noted that the methyl group at the benzylic site was attacked by cobalt(III) acetate, while the tertiary allylic hydrogen was not converted at all.

Similar results were obtained in the oxidation of (16c). Oxidation of (16c) gave only (18c) in good yield and (17c) was not formed at all. All the results demonstrate that tertiary allylic hydrogen cannot be oxidized by cobalt(III) acetate.

Oxidation of 1-Phenyl-2-methylpropene Derivatives (20).— The more substituted olefins (20) were oxidized under similar conditions in order to examine the effect of position of substituent on the product distribution. Table 5 lists the results.
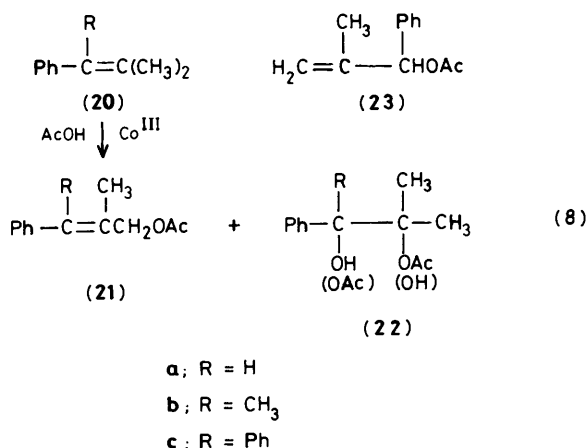
Oxidation of 2-methyl-1-phenylprop-1-ene (20a) gave both 3-acetoxy-2-methyl-1-phenylpropene (21a) and 1-acetoxy-2-propan-2-ol (22a) with predominant formation of the latter. In addition to these products, 3-acetoxy-2-methyl-3-phenylprop-1-ene (23) and benzaldehyde were formed in low yields. This result seems to show that more substituents favour the formation of glycol monoacetate.

2-Methyl-3-phenylbut-2-ene (20b) was oxidized much more quickly than (20a) to give a mixture of 3-acetoxy-3-methyl-2-phenylbutan-2-ol and 3-acetoxy-2-methyl-3-phenylbutan-2-ol (22b) as the main product with a small amount of 1-acetoxy-2-

Table 5. Oxidation of 2-methyl-1-phenylprop-1-ene derivatives (20)[a] by cobalt(III) acetate in acetic acid

[Olefin]$_0$/M	[Co^{III}]$_0$/M	Temp. (°C)	Time (h)	Recovered olefin (mole %)	Products (mole %)		
					(21)	(22)	PhCOR
R = H							
0.100	0.200	60	1	37	10	33	1.5[b]
0.100	0.200	80	4	11	14	48	4.8[b]
R = CH$_3$							
0.0406	0.0812	60	1	48	3.3	27	4.8
0.0406	0.0812	60	3	25	6.9	35	15
R = Ph							
0.107	0.214	60	1	23	34	35	2.4
0.107	0.214	60	4	6.0	41	37	5.3

[a] PhC(R)=C(CH$_3$)$_2$. [b] PhCH(OAc)–C(CH$_3$)=CH$_2$ was obtained (ca. 4—6% yield).

R
|
Ph—C=C(CH$_3$)$_2$

(20)

AcOH | Co^{III}

CH$_3$ Ph
| |
H$_2$C=C——CHOAc

(23)

R CH$_3$
| |
Ph—C=CCH$_2$OAc   +   Ph—C——C—CH$_3$ (8)
                        | |
                        OH   OAc
                        (OAc) (OH)

(21)   (22)

a; R = H
b; R = CH$_3$
c; R = Ph

methyl-3-phenylbut-2-ene (21b). Compound (22b) easily underwent further oxidation and considerable amounts of acetophenone were obtained in addition to (21b) and (22b). The result is reasonable since the replacement of benzylic hydrogen by a methyl group accelerated the formation of glycol monoacetate in the oxidation of (7) and (11).

Oxidation of 2-methyl-1,1-diphenylprop-1-ene (20c) gave both 3-acetoxy-2-methyl-1,1-diphenylprop-1-ene (21c) and a mixture of 2-acetoxy-2-methyl-1,1-diphenylpropan-1-ol and 1-acetoxy-2-methyl-1,1-diphenylpropan-2-ol (22c) with slightly predominant formation of (22c). This was the reverse expectation from the results in oxidations of (20a and b).

Discussion

Aliphatic and alicyclic olefins are oxidized by cobalt(III) acetate in acetic acid to give selectively allylic acetates.[5,6] On the other hand, oxidation of aromatic olefins affords two types of products, glycol monoacetate and allylic acetate. When the olefin has no allylic hydrogen, of course, only glycol monoacetate can be obtained in good yields.[2—4] When it has allylic hydrogens, the ratio of glycol monoacetate to allylic acetate in the product drastically changed according to the structure of the original olefins.

The treatment of (7a) with cobalt(III) acetate in acetic acid under nitrogen gave (8a) in good yield and (9a) was scarcely formed. Similar results were obtained in the oxidation of (11a) with the same oxidant. In effect, when R in aromatic olefins is hydrogen, allylic oxidation rather than 1,2-addition across the
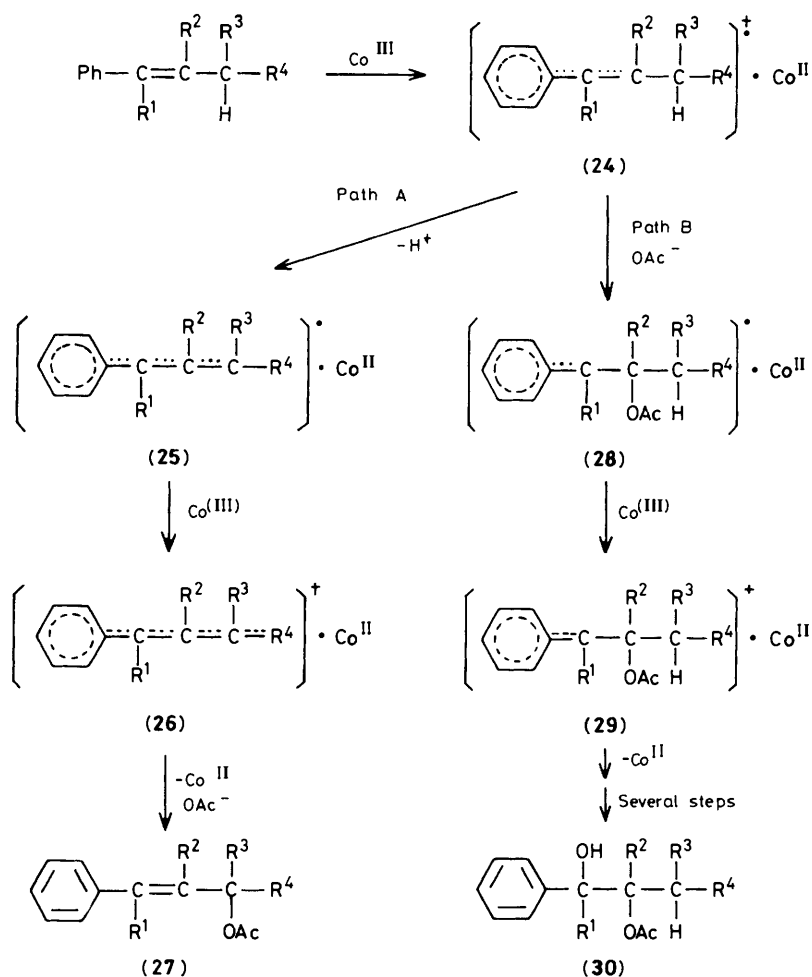
double bond is favoured. In contrast to these results, when the benzylic hydrogen was replaced by a methyl group, allylic oxidation was drastically retarded and the 1,2-addition reaction became faster. As shown in Tables 2 and 3, both (7b) and (11b) were oxidized by cobalt(III) acetate, giving preferentially (9b) and (13b), respectively.

The favourable formation of glycol monoacetate may be expected in the oxidation of (20a), since it is a trisubstituted olefin such as (7b) and (11b). Indeed, oxidation gave more (22a) than (21a), showing that the formation of glycol monoacetate is favoured in the oxidation of trisubstituted (and of course, tetrasubstituted) olefins regardless of the position of the substituents.

Similar results were obtained in the oxidation of 1,1-diphenyl derivatives of these systems. Although there were some differences in the product distributions between oxidations of (7c) and (11c), the replacement of the benzylic hydrogen in aromatic olefins by a phenyl group accelerated the 1,2-addition reaction in both cases. The favourable formation of a mixture of (2) and (3) over (3) and (4) in the oxidation of (1) is also reasonable since the olefin has a substituted or branched benzylic carbon.

These observations can be summarized as (a) the oxidation of disubstituted aromatic olefins (7a) and (11a) having allylic hydrogens favoured allylic oxidation except for the case of (16a) which has a tertiary allylic hydrogen and (b) the oxidation of higher-substituted aromatic olefins preferred the 1,2-addition reaction rather than allylic oxidation regardless of the position of substituents.

There are some reports that oxidation of organic compounds by cobalt(III) acetate in acetic acid proceeds via an one-electron abstraction by the oxidant to give a radical-cation. The initiation in autoxidation of alkylbenzenes catalysed by a relatively high concentration of cobalt(III) acetate is known to proceed through this path. The direct oxidation of organic compounds by the oxidant under nitrogen is successfully interpreted in terms of this mechanism.[8] Furthermore, radical-cations have been detected in e.s.r. studies of oxidation of aromatic compounds[9,10] and some highly substituted olefins[11] by cobalt(III) acetate in trifluoroacetic acid or acetic acid containing trifluoroacetic acid and boron trifluoride. All of these facts may demonstrate that both allylic oxidation and 1,2-addition are initiated by one-electron abstraction from olefins to give a radical-cation. The intervention of a radical-cation has been suggested for oxidation of olefins by cobalt(III) sulphate in aqueous acidic media[12] and by cobalt(III) trifluoroacetate in trifluoroacetic acid[13] However, little is known about the reaction mechanism in detail since these oxidants were too power-

Ph—C=C—C—R⁴ $\xrightarrow{Co^{III}}$ (24)

Path A −H⁺

Path B OAc⁻

(25) Co(III)

(28) Co(III)

(26) −Co II OAc⁻

(29) −Co II Several steps

(27)

(30)

Scheme.

ful to give relatively unstable transient compounds with the exception of carboxylic acids.

We have already observed that allylic oxidation of alkyl-substituted aliphatic and alicyclic olefins by cobalt(III) acetate gave only one allylic acetate regioselectively, with the acetoxy group introduced at the site furthest from the substituent,[1,6] that (9a) was obtained with slight retention of configuration in oxidation of (7a),[3] and that no rearranged product was observed in oxidation of some olefins even if it was a rearrangement-prone olefin.[1,2] These results can be well explained by the assumption of the presence of a Co-co-ordinated intermediate during the reaction.[1,2] The cobalt ion may depart from the organic part of intermediate synchronous with or just before the introduction of the final attacking species.

On the basis of the above discussion, the mechanism in the Scheme can be suggested for the oxidation of olefins with cobalt(III) acetate in acetic acid under nitrogen. Further evidence for the presence of a radical-cation comes from the inertness of tertiary allylic hydrogens towards cobalt(III) acetate oxidation. The oxidation of both (7a) and (11a) gave predominantly the allylic acetates (8a) and (12a), respectively, as the main products. On the other hand, only (18a) was obtained and no (17a) was obtained on oxidation of (16a). Thus, the reactivity of allylic hydrogen may be described as follows: PhCH=CHCH₂CH₃ > PhCH=CHCH₃ ≫ PhCH= CHCH(CH₃)₂. This order is supported by the facts that (19) was obtained but no (17b) in the oxidation of (16b) and the oxidation of (16c) gave only (18c), since the yields of (8b) and

(12b) were always higher than those of (10) and (14) in oxidations of (7b) and (11b), respectively.

Generally, the reactivity of C–H bonds for oxidation involving hydrogen abstraction from benzylic and allylic sites is as follows order: tertiary > secondary > primary.[14] Since this order is completely different from the above, the direct hydrogen-abstraction mechanism from the allylic site could be excluded. However, an order similar to that obtained in the present reaction has been observed in the stoicheiometric oxidation of alkylbenzenes by cobalt(III) acetate[8,15] and cobalt(III) acetate-catalysed autoxidation of alkylbenzenes.[9] In the stoicheiometric oxidation, the reactivity of toluene is tenfold greater than that of cumene and in catalysed autoxidation the relative rate per hydrogen is reported to be as follows: toluene:ethylbenzene:isopropylbenzene = 1.0:1.3:0.3.[9] From these observations, the present reaction was considered to involve the same intermediate as the oxidation of alkylbenzenes. For the oxidation of alkylbenzenes and olefins, the following intermediates (31) and (32) were postulated.

(31)

(32)
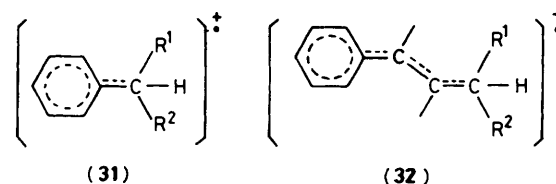
When intermediates (31) and (32) were compared, there appeared to be some similarity between radical-cations derived from cumene and aromatic olefins with a tertiary allylic hydrogen atom. The similarity allows us to conclude that allylic oxidation also proceeds via the same radical-cation mechanism as that suggested for oxidation of alkylbenzene.

The radical-cation (24) formed by a one-electron transfer may be consumed by two competitive reactions. (a) It loses a proton to form an allylic radical, which is further oxidized to the allylic cation followed by addition of acetate ion, and (b) it is directly attacked by an acetoxy ion before departure of a proton, followed by oxidation by cobalt(III) acetate and then addition of hydroxide ion. The former path gives allylic acetate and the latter gives glycol monoacetate.

There is no doubt that the radical-cation formed in the first step must contribute to the determination of the product distribution, since two paths are considered to proceed through the intermediate. The allylic radical (25) may be more stable than the radical-cation (24) because of its prolonged conjugation. Thus, the latter has a tendency to change to the former. In this case, the reaction goes through path A and the allylic acetate may be obtained predominantly, and the glycol monoacetate may not be formed.

A crowded radical-cation formed from highly substituted olefins may be more stable than a less substituted one because the methyl or phenyl group can stabilize the radical cation by electron-donating power and conjugation. The stabilized radical-cation, then, may exist longer without the departure of an allylic proton and thus there is enough time to react with acetate ion (probably a ligand of cobalt ion). In this case, the reaction takes path B and the yield of glycol monoacetate should increase at the expense of allylic acetate.

This behaviour agrees with the facts that only allylic acetate was obtained in the oxidation of aliphatic and alicyclic olefins, 1,2-addition along with allylic oxidation always occurs in aromatic olefins, and the yield of glycol monoacetate increases with an increase in the number of substituents on the double bond.

Oxidation of (20c) gave comparable amounts of (21c) and (22c), although the high ratio of (22c)/(21c) was expected since two phenyl groups may stabilize the radical-cation intermediate. However, there is steric hindrance between the two phenyl groups in the radical-cation and they cannot, at the same time, lie in a plane with the double bond. This may destabilize the radical-cation and thus give a considerable amount of allylic acetate.

There are many studies of the mechanism of oxidation of olefin by various metal salts. The mechanism can be divided into three categories: (a) the formation of cyclic intermediates in oxidation by $KMnO_4$,[16] and chromium compounds,[17] (b) oxymetallation–demetallation in lead(IV),[18] mercury(II),[19] thallium(III),[20] and palladium(II),[21] and (c) the formation of alkyl radicals by degradation of oxidant as for Mn^{III}[22] and Ce^{IV}.[23] The present mechanism is specific to the oxidation of olefins by cobalt(III) ions.

Experimental

^{1}H N.m.r. spectra were recorded in $CDCl_3$ or CCl_4 on a JEOL model PMX-60 or JNM-C-HL spectrometer. I.r. spectra were determined for liquid films or KBr disks on a JASCO DS-403G spectrophotometer. G.l.c. was carried out on Shimadzu GC-6A and GC-4C instruments with a 2 m glass column packed with 5% PEG-20M on Chromosorb W-DMCS or a 2 m glass column packed with 1% Silicone OV-17 on Chromosorb W-DMCS. For the measurements of yields, appropriate internal standards were 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 or 30% Silicone SE-30 on Celite 545, attached to a Shimadzu APP-5 fraction collector through a glass joint.

Starting Materials.—Cobalt(III) acetate was prepared by bubbling ozone into a solution of commercial cobalt(II) acetate tetrahydrate in acetic acid in the presence of acetic anhydride.[24] Olefins were made by as follows.[25] Phenyl-magnesium halide was treated with aldehydes, ketones, or esters in ether to obtain aromatic alcohols. The alcohols formed were dehydrated by refluxing with concentrated sulphuric acid[26] or over potassium hydrogensulphate[27] to give olefins. The olefins were purified by distillation or, if necessary, by preparative g.l.c. Olefins used for reaction were confirmed to be over 99% pure by g.l.c. analysis. The structure of olefins was determined by n.m.r. spectra.

Oxidation Procedure.—Weighed olefin was mixed with cobalt(III) acetate solution in acetic acid (5 ml) in a flask equipped with a glass stopper. The reaction vessel was flushed with dry nitrogen gas, and then kept at constant temperature in a thermostat without agitation. After the addition of an internal standard, the solution was poured into water (ca. 30 ml) and extracted with ether (3 × 10 ml). The combined ethereal solution was washed successively with brine, 10% aqueous sodium carbonate, and brine, and dried over anhydrous sodium or magnesium sulphate. After filtration, the ether was removed on a rotary evaporator to leave a pale-yellow oil, which was analysed by g.l.c. Reaction products were identified from their retention times of g.l.c.

Reference Compounds.—A mixture of 2-acetoxy-1-phenyl-cyclohexanol (2) and 2-acetoxy-2-phenylcyclohexanol (3) was prepared by epoxidation of (1) with peracetic acid followed by acetolysis in acetic acid, m.p. 114—115 °C.[28] 3-Acetoxy-1-phenylcyclohexene (4) and 6-acetoxy-1-phenylcyclohexene (5) were made by chromic acid oxidation of (1),[29] followed by reduction with lithium aluminium hydride in ether[30] and then acetylation with acetic anhydride and sodium acetate. Biphenyl was a commercial reagent. Other reference samples were prepared by the reaction of olefins with cobalt(III) acetate.

Oxidation of (E)-2-*Phenylbut-2-ene* (7b).—Compound (7b) was treated with cobalt(III) acetate in acetic acid under nitrogen. The same treatment of the reaction mixture as described in the reaction procedure gave an oil, which was separated by preparative g.l.c. to give (10), (8b), and (9b).

1-Acetoxy-2-phenylbut-2-ene (10): δ($CDCl_3$) 7.25 (5 H, s), 5.73 (1 H, q), 5.20 (2 H, s), 1.91 (3 H, s), and 1.30 (3 H, d).

1-Acetoxy-3-phenylbut-2-ene (8b): δ($CDCl_3$) 7.24 (5 H, s), 6.40 (1 H, d), 5.80 (2 H, m), and 2.0—1.9 (6 H, m).

3-Acetoxy-2-phenylbutan-2-ol (9b): δ($CDCl_3$) 7.3—7.0 (5 H, m), 5.07 (1 H, q), 3.0 (1 H, s), 1.98 (3 H, s), 1.53 (3 H, s), and 1.1 (3 H, d).

Oxidation of 1,1-*Diphenylprop-1-ene* (7c).—Oxidation of (7c) by cobalt(III) acetate and the same treatment as above gave a solid, which was recrystallized from n-hexane to afford needles of (9c). The filtrate from recrystallization was evaporated to leave a viscous liquid, which was separated by preparative g.l.c. using a Silicone SE-30 column, giving (8c). 2-Acetoxy-1,1-diphenylpropanol (9c): δ($CDCl_3$) 7.25 (10 H, m), 5.90 (1 H, q), 2.70 (1 H, s), 1.82 (3 H, s), and 1.21 (3 H, d). 3-Acetoxy-1,1-diphenylprop-1-ene (8c): δ($CDCl_3$) 7.25 (10 H, s), 6.2 (1 H, t), 4.7 (2 H, d), and 2.01 (3 H, s).

Oxidation of (E)-1-*Phenylbut-1-ene* (11a).—Oxidation of (11a) by cobalt(III) acetate and the same treatment as above

gave an oil, which was separated by preparative g.l.c. using a PEG-20M column to give (12a) and (13a). 3-Acetoxy-1-phenyl-but-1-ene (12a): $\delta(CCl_4)$ 7.22 (5 H, s), 6.50 (1 H, d), 6.00 (1 H, q), 5.40 (1 H, m), 2.00 (3 H, s), and 1.40 (3 H, d); $v_{max.}$ (thin film) 1 720, 1 450, and 1 370 cm^{-1}. 2-Acetoxy-1-phenylbutan-1-ol (13a): $\delta(CCl_4)$ 7.2 (5 H, m), 5.48 (d), 4.89 (q), 4.50 (d), and 3.69 (q) (total 2 H), 3.19 (1 H, s), 2.00 (3 H, s), 1.30 (2 H, m), and 0.88 (3 H, t); $v_{max.}$ (thin film) 3 400, 1 730, 1 460, and 1 380 cm^{-1}. These data show that compound (13a) is a mixture of 2-acetoxy-1-phenylbutan-1-ol and 1-acetoxy-1-phenylbutan-2-ol.

Oxidation of 2-Phenylpent-2-ene (11b).—Oxidation of (11b) by cobalt(III) acetate and the same procedure as above gave an oil. After distillation in a glass tube oven, the oil obtained was separated by column chromatography using silica gel and n-hexane–ethyl acetate to afford (12b) and (13b). 4-Acetoxy-2-phenylpent-2-ene (12b): $\delta(CCl_4)$ 7.22 (5 H, s), 5.65 (2 H, m), 2.11 (3 H, s), 2.03 (3 H, s), and 1.41 (3 H, d). 3-Acetoxy-2-phenylpentan-2-ol (13b): $\delta(CCl_4)$ 7.2 (5 H, m), 5.10 (1 H, q), 2.60 (1 H, s), 1.93 (3 H, s), 1.65 (2 H, m), 1.40 (3 H, s), and 0.81 (3 H, t).

1-Acetoxy-2-phenylpent-2-ene (14) was prepared by refluxing (11b) with selenium dioxide in acetic anhydride. The same procedure as that of cobalt(III) acetate oxidation gave an oil which was purified by preparative g.l.c., $\delta(CCl_4)$ 7.20 (5 H, s), 5.70 (1 H, t), 4.70 (2 H, s), 2.00 (4 H, s), and 0.98 (3 H, t).

Oxidation of 1,1-Diphenylbut-1-ene (11c).—Oxidation of (11c) by cobalt(III) acetate and the same procedure as above gave a solid, which recrystallized from n-hexane to give needles of (13c), $\delta(CDCl_3)$ 7.2—7.0 (10 H, m), 5.92 (1 H, q), 2.72 (1 H, s), 1.92 (3 H, s), 1.55 (2 H, m), and 0.83 (3 H, t); $v_{max.}$ (KBr disk) 3 400, 1 730, 1 440, and 1 360 cm^{-1}. 1,2-Diacetoxy-1,1-di-phenylbutane (15) was prepared by the acetylation of (13c), $\delta(CDCl_3)$ 7.2 (10 H, m), 6.30 (1 H, q), 0.89 (3 H, t), and 2.0—1.9 (9 H, m).

As (12c) was not obtained by the reaction of (11c) with cobalt(III) acetate, it was prepared as follows. To methyl-magnesium iodide in ether was added β,β-diphenylacryl-aldehyde. After the addition of ammonium chloride in water, the ethereal solution was separated and dried (Na$_2$SO$_4$). After filtration, the ether was removed to leave an oil, which was acetylated, without purification, with acetic anhydride and pyridine. The product was poured into water and extracted with ether. The ethereal solution was washed with dilute hydrochloric acid and water, and then dried (Na$_2$SO$_4$). After filtration, the ether was evaporated to afford an oil, which was column chromatographed using silica gel and n-hexane, $\delta(CCl_4)$ 7.2 (10 H, s), 6.00 (1 H, d), 5.35 (1 H, m), 1.93 (3 H, s), and 1.30 (3 H, d).

Oxidation of 3-Methyl-1-phenylbut-1-ene (16a).—The reaction of (16a) with cobalt(III) acetate was too slow to obtain products for identification and for making a calibration curve. Hence, authentic samples were made as follow.

Compound (16a) was treated with silver acetate and iodine in wet acetic acid (wet Prevo'st reaction). The product was poured into water and extracted with ether. The ethereal solution was washed with 10% aqueous sodium carbonate and water, and dried (Na$_2$SO$_4$). After filtration, the ether was removed on a rotary evaporator to leave an oil, which was purified by column chromatography using silica gel and n-hexane–ethyl acetate. A mixture of 2-acetoxy-3-methyl-1-phenylbutan-1-ol and 1-acetoxy-3-methyl-1-phenylbutan-2-ol (18a) was obtained: $\delta(CCl_4)$ 7.25—7.0 (5 H, m), 5.46 and 4.47 (total 1 H, q), 4.70 and 3.44 (total 1 H, d), 2.8—2.5 (1 H), 1.92 and 1.86 (total 3 H, s), 2.0—1.2 (1 H), 0.87 and 0.84 (total 6 H, d), $v_{max.}$ (thin film) 3 400, 1 730, 1 450, and 1 360 cm^{-1}.

Oxidation of (E)-4-Methyl-2-phenylpent-2-ene (16b).—Compound (16b) was treated with cobalt(III) acetate in acetic acid. The product was obtained by the same procedure as described above and purified by column chromatography using silica gel and n-hexane–ethyl acetate. 3-Acetoxy-4-methyl-2-phenylpentan-2-ol (18b) was obtained: $\delta(CCl_4)$ 7.25—7.0 (5 H, m), 4.88 (1 H, d), 2.60 (1 H, s), 1.87 (3 H, s), 1.47 (3 H, s), 2.0—1.3 (1 H), and 0.85 and 0.72 (6 H, d); $v_{max.}$ (thin film) 3 300, 1 730, 1 450, and 1 370 cm^{-1}.

1-Acetoxy-4-methyl-2-phenylpent-2-ene (19) was not obtained from cobalt(III) acetate oxidation of (16b) but was prepared by selenium dioxide oxidation of (16b) in acetic anhydride. The product was isolated with the same procedure as described above and purified by column chromatography using silica gel and n-hexane–ethyl acetate, $\delta(CCl_4)$ 7.2 (5 H, s), 5.30 (1 H, d), 5.06 (2 H, s), 2.00 (3 H, s), 1.4—1.2 (1 H), and 0.80 (6 H, d).

Oxidation of 3-Methyl-1,1-diphenylbut-1-ene (16c).—Compound (16c) was treated with cobalt(III) acetate in acetic acid. The product was isolated with the same procedure as described above and purified by recrystallization from n-hexane to give 2-acetoxy-3-methyl-1,1-diphenylbutan-1-ol (18c): $\delta(CDCl_3)$ 7.3—7.0 (10 H), 5.92 (1 H, d), 2.62 (1 H, s), 1.94 (3 H, s), 1.5—1.0 (1 H), and 1.0 and 0.83 (6 H, d).

Oxidation of 2-Methyl-1-phenylprop-1-ene (20a).—Compound (20a) was treated with cobalt(III) acetate in acetic acid. The product was isolated with the same method as described above and the resulting oil was distilled on a glass tube oven. The fraction of b.p. 90—95 °C at 24 mmHg was separated by column chromatography using silica gel. Three fractions were obtained by changing eluant from n-hexane, through n-hexane–ethyl acetate (8:2), to ethyl acetate. Evaporation of the solvent from the first fraction gave 3-acetoxy-2-methyl-3-phenylprop-1-ene (23), $\delta(CCl_4)$ 7.25 (5 H, s), 6.03 (1 H, s), 5.0 (1 H, s), 4.87 (1 H, m), 2.00 (3 H, s), and 1.61 (3 H, d); $v_{max.}$ (thin film) 1 740, 1 450, and 1 370 cm^{-1}.

That from the second fraction gave 3-acetoxy-2-methyl-1-phenylprop-1-ene (21a), $\delta(CCl_4)$ 7.23 (5 H, s), 6.40 (1 H, m), 4.50 (2 H, s), 2.03 (3 H, s), and 1.84 (3 H, d); $v_{max.}$ (thin film) 1 730, 1 440, and 1 380 cm^{-1}.

That from the third fraction gave 1-acetoxy-2-methyl-1-phenylpropan-2-ol (22a), $\delta(CDCl_3)$ 7.2—7.0 (5 H, m), 5.43 (1 H, s), 2.10 (1 H, s), 2.00 (3 H, s), and 1.09 (6 H, s); $v_{max.}$ (thin film) 3 420, 1 730, 1 450, and 1 300 cm^{-1}.

Oxidation of 2-Methyl-3-phenylbut-2-ene (20b).—Compound (20b) was treated with cobalt(III) acetate and the same work-up as described above gave an oil, which was chromatographed using silica gel. Two fractions were obtained by changing developing solvent from n-hexane–ethyl acetate (8:2) to ethyl acetate. Evaporation of the solvent from the first eluant gave 1-acetoxy-2-methyl-3-phenylbut-2-ene (21b), $\delta(CCl_4)$ 7.23 (5 H, s), 4.35 (2 H, s), 2.00 (3 H, s), 1.95 (3 H, s), and 1.83 (3 H, s); $v_{max.}$ (thin film) 1 740, 1 440, and 1 370 cm^{-1}.

The same treatment of the second eluant gave a mixture of 3-acetoxy-3-methyl-2-phenylbutan-2-ol and 3-acetoxy-2-methyl-3-phenylbutan-2-ol (22b), $\delta(CCl_4)$ 7.3—7.0 (5 H, m), 3.1—2.7 (1 H), and 2.09, 1.99, 1.93, 1.59, 1.48, 1.38, 1.15, and 1.09 (total 9 H, s); $v_{max.}$ (thin film) 3 430, 1 730, 1 450, and 1 370 cm^{-1}.

Oxidation of 2-Methyl-1,1-diphenylprop-1-ene (20c).—Compound (20c) was treated with cobalt(III) acetate in acetic acid. After work-up as described above, the resulting crude material was distilled in a glass tube oven (120 °C; 3 mmHg) and then was separated with column chromatography using silica gel. Two fractions were obtained by using the solvent from n-hexane–ethyl acetate (9:1) to ethyl acetate. Evaporation of the solvent from the first eluant gave 3-acetoxy-2-methyl-1,1-

diphenylprop-1-ene (**21c**), δ(CCl₄) 7.25 (5 H, s), 4.60 (2 H, s), 2.03 (3 H, s), and 1.83 (3 H, s); $v_{max.}$ (thin film) 1 730, 1 450, and 1 380 cm⁻¹.

The same procedure from the second fraction gave 2-acetoxy-2-methyl-1,1-diphenylpropan-1-ol (**22c**), δ(CCl₄) 7.3—7.0 (10 H, m), 4.68 (1 H, s), 1.85 (3 H, s), and 1.53 (6 H, s); $v_{max.}$ (KBr disk) 3 400, 1 740, 1440, and 1 370 cm⁻¹.

References

1 Part 7, M. Hirano and T. Morimoto, preceding paper.
2 M. Hirano and T. Morimoto, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1033.
3 M. Hirano and T. Morimoto, *J. Chem. Res.,* 1979, (*S*) 104; (*M*) 1069.
4 M. Hirano, E. Kitamura, and T. Morimoto, *J. Chem. Soc., Perkin Trans. 2*, 1980, 569.
5 L. Verstraelen, M. Lalmand, A. J. Hubert, and P. Teyssie, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1285.
6 M. Hirano, K. Nakamura, and T. Morimoto, *J. Chem. Soc., Perkin Trans. 2*, 1981, 817.
7 R. Crigee, 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York, 1965, p. 277.
8 R. A. Sheldon and J. K. Kochi, 'Metal-catalysed Oxidation of Organic Compounds,' Academic Press, New York, 1981, p. 120.
9 E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.,* 1969, **91**, 6830.
10 R. M. Dessau, *J. Am. Chem. Soc.,* 1970, **92**, 6356.
11 R. M. Dessau, S. Shih, and E. I. Heiba, *J. Am. Chem. Soc.,* 1970, **92**, 412.
12 C. E. H. Bawn and J. A. Sharp, *J. Chem. Soc.,* 1959, 1854, 1866.
13 T. Tang and J. K. Kochi, *J. Inorg. Nucl. Chem.,* 1973, **35**, 3845.
14 (*a*) W. A. Pryor, 'Free Radicals,' McGraw-Hill, New York, 1966, p. 149; (*b*) Y. Kamiya, *J. Catal.,* 1974, **33**, 480.
15 A. Onopchenko, J. G. D. Schulz, and R. Seekircher, (*a*) *Chem. Commun.,* 1971, 939; (*b*) *J. Org. Chem.,* 1972, **37**, 2564; (*c*) A. Onopchenko and J. G. D. Schulz, *ibid.,* 1972, **37**, 2564; (*d*) E. Baciocchi, L. Mandolini, and C. Rol, *ibid.,* 1980, **45**, 3906.
16 R. Stewart, 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York, 1965, p. 1.
17 K. B. Wiberg, 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York, 1965, p. 69.
18 (*a*) H. J. Kabbe, *Justus Liebigs Ann. Chem.,* 1976, **204**, 656; (*b*) A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1,* 1974, 1923; R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. B*, (*c*) 1967, 771; (*d*) 1968, 994; (*e*) K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.,* 1964, **29**, 3353; (*f*) G. H. Whitham, *J. Chem. Soc.,* 1961, 2232; (*g*) A. Lethbridge, R. O. C. Norman, C. B. Thomas, and W. J. E. Parr, *J. Chem. Soc., Perkin Trans. 1,* 1975, 231; (*h*) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.,* 1968, **90**, 2706.
19 (*a*) Z. Rappoport, L. K. Dyall, S. Winstein, and W. G. Young, *Tetrahedron Lett.,* 1970, 3483; (*b*) Z. Rappoport, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.,* 1972, **94**, 2320; (*c*) W. Treibs and H. Bast, *Justus Liebigs Ann. Chem.,* 1949, **561**, 165.
20 (*a*) R. J. Quellette, G. Kordosky, C. Levin, and S. Williams, *J. Org. Chem.,* 1969, **34**, 4104; (*b*) J. B. Lee and M. J. Price, *Tetrahedron,* 1964, **20**, 1017.
21 (*a*) W. Kithing, Z. Rappoport, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.,* 1966, **88**, 1054; (*b*) S. Wolfe and G. C. Campbell, *ibid.,* 1971, **93**, 1497.
22 (*a*) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.,* 1968, **90**, 5905; (*b*) J. B. Bush, Jr., and H. Finkbeiner, *ibid.,* p. 5903; (*c*) J. R. Gilmore and J. M. Mellor, *J. Chem. Soc. C,* 1971, 2355.
23 E. I. Heiba and R. M. Dessau, *J. Am. Chem. Soc.,* 1970, **92**, 995.
24 (*a*) E. Koubek and J. O. Edwards, *J. Inorg. Nucl. Chem.,* 1963, **25**, 1401; (*b*) S. S. Lands, C. D. Falk, and J. K. Kochi, *ibid.,* 1971, **33**, 4101.
25 W. S. Emerson, *Chem. Rev.,* 1949, **45**, 347.
26 J. F. Norris, *Org. Synth.,* 1941, Coll. Vol. I, p. 430.
27 C. G. Overberger and J. H. Saunders, *Org. Synth.,* 1955, Coll. Vol. III, p. 204.
28 R. E. Lyle and G. G. Lyle, *J. Org. Chem.,* 1953, **18**, 1058.
29 D. Ginsbury and R. Rappo, *J. Chem. Soc.,* 1951, 517.
30 G. F. Woods, *J. Am. Chem. Soc.,* 1948, **70**, 2174.