Oxidation by Cobalt(III) Acetate. Part 2.[1] Oxidation of Styrene in Acetic Acid

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The oxidation of styrene with cobalt(III) acetate has been studied in acetic acid under nitrogen. The product distribution is greatly affected by the composition of the solvent; in acetic acid and in wet acetic acid the reaction exclusively leads to 1,2-addition products, whereas in dry acetic acid preconditioned with acetic anhydride extensive formation of radical products is observed. None of the conditions gave rise to a rearrangement product. A Co-co-ordinated intermediate is proposed for the formation of 1,2-addition products.

THE oxidation of olefins by various metal acetate oxidants, e.g. Pb^{IV},[2-5] Hg^{II},[2,3,6,7] Tl^{III},[2,3,8] Mn^{III},[9-11] Ce^{IV},[12] etc., have recently attracted much attention. In the reactions with these oxidants the mechanisms can be conveniently classified into two types. For example, Pb^{IV}, Hg^{II}, and Tl^{III} electrophilically add to olefins to form organometallic compounds. In the case of Hg^{II} the adducts are quite stable, whereas Pb adducts are

reaction, leading to the addition of a methyl and a acetoxy-group across the double bond.

It has recently been reported that cobalt salts are potent reagents for the oxidation of various compounds, e.g. aldehydes,[13-15] alcohols,[15] alkanes,[16-19] alkylaromatics,[20-23] olefins,[15,24,25] etc. On the basis of kinetic results, the oxidation with cobalt(III) acetate has been considered to occur via an electron-transfer mechanism.[15-17,23] In a

TABLE 1

Distribution of products from the oxidation of styrene with cobalt(III) acetate in acetic acid at 60 °C [a]

Expt. no.	$[Co^{III}]_0$ (M)	$[Styrene]_0$ (M)	$[Co^{III}]:[St]$ (mol. ratio)	Time (h)	(1) [b]	Products (mol %)				
						(2)	(3)	(4) + (5)	(6)	(7)
1	0.2212	0.2212	1	42	50	1.8	0.8	38	3.4	2.1
2	0.2212	0.1106	2	6	40	1.4	1.0	37	0.8	2.4
3	0.2212	0.1106	2	12	19	1.8	1.3	66	1.5	2.1
4	0.2212	0.1106	2	42	12	2.7	1.2	75	5.7	5.3
5	0.2212	0.1106	2	72	4.3	2.2	1.3	75	8.6	4.3
6	0.2212	0.0737	3	42	3.2	2.3	1.9	77	7.2	11
7	0.2212	0.0553	4	42	0.6	1.6	2.3	80	7.8	7.1

[a] Under N_2. [b] Recovered styrene in mol %.

too unstable to be isolated, resulting in the formation of 1,2-addition and allylic and skeletal rearrangement products. The Tl adducts, though unstable, can be sometimes isolated under favourable conditions. A general scheme for the formation of 1,2-addition products in which the reaction is considered as ionic is illustrated in Scheme 1. The reaction consists of (i) formation of an organometallic compound from olefin and oxidant, (ii) heterolytic metal–carbon cleavage to give a carbocation, and (iii) addition of a nucleophile to the resulting cation.
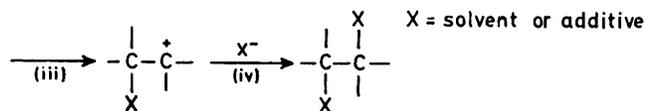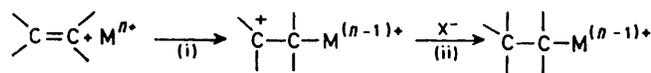
In contrast, Mn^{III} and Ce^{IV} acetates thermally decompose to generate a carboxymethyl radical, giving eventually γ-lactones (considered as a radical reaction). In the Pb^{IV} system, depending on the conditions, the radical reaction occurs competitively with an ionic

SCHEME 1

limited number of cases, a radical cation has been detected by e.s.r. spectroscopy.[21,26] However, there is little detailed information on the reaction intermediates and products for the oxidation of olefins.

In our previous paper,[1] we reported the oxidation of α- and cis- and trans-β-methylstyrene with cobalt(III) acetate in acetic acid. The present study was undertaken in order to elucidate the reaction mechanism for the oxidation of styrene in acetic acid. The effect of solvent, reaction temperature, and acetate ion on the product distribution has also been investigated.

RESULTS AND DISCUSSION

Styrene was easily oxidized at 60 °C giving six products: benzaldehyde (2), benzylidene diacetate (3), 1-phenylethane-1,2-diol 1-acetate (4) and 2-acetate (5), 1-phenylethane-1,2-diol diacetate (6), and benzoic acid (7). The results are presented in Table 1.

The major products, the glycol monoacetates (4) and (5), are known to be interconvertible via the intermediate (8) even at room temperature [27] and because of this we were unable to establish an exact product ratio for them by the present techniques. The glycol monoacetates appeared as one peak on g.l.c. analysis, so that these were estimated as a single group.

Further oxidation of primary products was unavoid-

able with prolonged reaction and cleavage products such as (2), (3), and (7) gradually increased with time. These products also increased when the ratio of the initial concentration of Co^{III} to that of styrene increased,

(Table 4). The yields of the glycol monoacetates increased in proportion to the amount of water added, whereas there was a remarkable decrease of them on addition of acetic anhydride.

TABLE 2
Oxidation of the products with cobalt(III) acetate ^{a}

Expt. no.	Substrates (M)	[Co^{III}]$_0$ (M)	Temp. (°C)	Time (h)	[Sub] ^{b}	Products (mol %)			
						(2)	(3)	(6)	(7)
8	(2) 0.1334	0.1334	70	47	36				60
9	(3) 0.0667	0.1334	80	21	73	4.4			19
10	(4) + (5) ^{c}	0.0467	80	4	88	2.4	0.2	3.5	17
11	(4) + (5) ^{c}	0.0467	80	22	55	1.5		12	37
12	(4) + (5) ^{c}	0.0467	80	48	23	1.0		21	58
13	(4) + (5) ^{c}		80	48	77			23	
14	(6) 0.0667	0.1334	80	21	93	5.2			
15	(9) 0.0667	0.1334	80	21	100				

^{a} In acetic acid under N$_2$. ^{b} Recovered substrates in mol %. ^{c} Initial concentration of a mixture of the glycol monoacetates was 0.0467M.

showing the compounds are secondary products which are presumably derived from (4), (5), and (6). Independent reactions of the compounds (4)—(6) with cobalt(III) acetate provide additional evidence for the hypothesis (Table 2).

Experiments 1, 4, 6, and 7 show that the sum of the

PhCHO   PhCH(OAc)$_2$ PhCH—CH$_2$ PhCH—CH$_2$
                                               | | | |
                                              OAc   OH   OH   OAc

(2)   (3)   (4)   (5)

PhCH—CH$_2$ PhCO$_2$H
      | |
     OAc   OAc

(6)   (7)
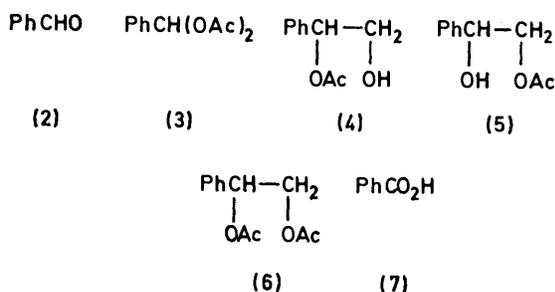
yields of the glycol monoacetates becomes almost constant at [Co^{III}]$_0$/[styrene]$_0$ $\simeq$ 2, indicating that the primary reaction follows the stoicheiometric relationship shown in equation (1).

Effect of Temperature.—The effect of temperature on product distribution was examined in the range 70—100 °C (Table 3). With increased temperature, a little

A notable feature in the product distribution in the dry system was the increased yield of methyl adduct and formation of the γ-lactone (10). These products are considered to be derived *via* a radical pathway.[4,11]

PhCH—CH$_2$
   /   \
  O   O   (8)
   \   /
    C
   /   \
  Me   OH
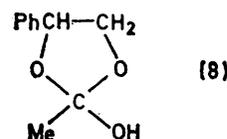
Hence it should be noted that both ionic and radical pathways proceed competitively in dry acetic acid.

Effect of Acetate Ion.—Although the remarkable acceleration of the reaction has been reported in the oxidation of alkylbenzenes with cobalt(III) acetate,[20,23]

PhCH=CH$_2$ + 2 Co^{III} $\longrightarrow$ [(4) + (5)]+ 2 Co^{II} (1)
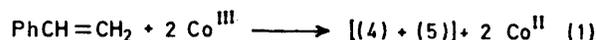
the present reaction was not so affected by the addition of acetate ion alone (Table 5). However, co-existence of acetic anhydride with a large amount of KOAc or NaOAc altered the nature of the reaction: in the dry system containing alkali acetates a radical pathway predominates over an ionic pathway.

TABLE 3
Effect of temperature on the product distribution ^{a}

Expt. no.	Temp. (°C)	Time (h)	(1) ^{b}	Products (mol %)					
				(2)	(3)	(4) + (5)	(6)	(7)	(9)
16	70	4	19	1.9	1.0	71	0.9	5.6	
17	70	22	7.9	4.7	1.0	73	5.6	5.8	
18	80	4	16	2.9	2.2	70	2.5	7.7	0.2
19	90	4	12	4.4	2.9	70	3.9	5.8	0.4
20	100	2	14	4.5	3.3	56	3.8	3.9	0.9
21	100	4	9.2	5.0	2.8	50	5.9	4.8	0.9

^{a} In acetic acid under N$_2$, [Co^{III}]$_0$ = 0.1584M, [styrene]$_0$ = 0.0797M. ^{b} Recovered styrene in mol %.

of the methyl adduct, 1-phenylpropyl acetate (9), was formed whilst formation of the glycol monoacetates dramatically decreased; formation of compounds (2), (6), and (7) increased at the expense of (4) and (5).

Effect of Solvent.—Product distribution was drastically affected by the addition of water or acetic anhydride

Mechanism.—The reaction in acetic acid and in wet acetic acid exclusively leads to 1,2-addition products, whereas in dry acetic acid preconditioned with acetic anhydride radical products are preferentially formed. These results can be explained in terms of competitive oxidation of styrene *versus* the cobalt ligand itself.

Formation of 1,2-*Addition Products.*—Although in comparison with lead(IV) acetate oxidations, it might appear not difficult, at first sight, to illustrate the reaction mechanism for the formation of 1,2-addition products in the present reaction, some modification of the

PhCHCH₂Me
|
OAc   (9)

PhCH—CH₂
  /   \
 O   CH₂   (10)
   \   /
    C
    ‖
    O
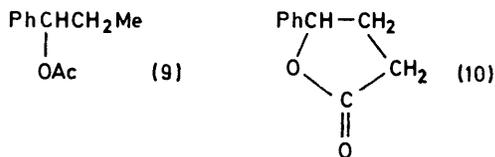
mechanism is required because of the absence of rearrangement products.

In the present reaction a cationic intermediate would be expected to react with the most accessible nucleophile, AcOH, to give the 1,2-diacetate (6). However,

still formed in an almost constant ratio irrespective of the concentration of acetic anhydride added (last column in Table 4). This indicates that adventitious water is not the sole source of hydroxy-groups. An alternative possibility for the formation of glycol monoacetates is the insertion of a cobalt OH-ligand as suggested recently in the literature.[25] However, the present results cannot be explained solely by a ligand-transfer mechanism, since the yield of (6) as well as the yield of (2) is too low compared with that of the glycol monoacetates; in addition, the glycol, phenylethylene glycol, was absent. We observed that glycols react readily with cobalt(III) acetate in acetic acid to afford exclusively cleavage compounds such as aldehydes or ketones. The third possibility for the formation of glycol monoacetates, that the diacetate (6) is hydrolysed during work-up and/or reaction, is ruled out, since (6) can be recovered essentially

TABLE 4

Effect of solvents on the product distribution [a]

Expt. no.	Temp. (°C)	Time (h)	Additives (M) H₂O	Ac₂O	(1) [b]	(2)	(3)	(4) + (5)	(6)	(7)	(9)	(10)	Mol ratio †
22 *	60	72			14	8.1	1.0	26	4.4	14			
23	60	72	0.05		6.1	6.0	0.8	50	6.3	12			
24	60	72	0.10		14	4.5	2.5	59	6.7	8.8			
25	60	72	0.20		9.5	4.8	Trace	73	8.7	8.8			
26	70	20		0.30	43	5.3	6.3	Trace	5.1	7.2	2.7	4.2	0.42
27	70	20		0.50	34	3.8	7.4		7.8	7.8	2.2	6.1	0.40
28	70	20		1.0	32	3.5	6.5		11	8.2	3.9	11	0.43
29	70	20		50% Ac₂O	37	1.8	2.5		13	7.8	1.7	24	0.40

[a] In acetic acid under N_2, $[Co^{III}]_0 = 0.100M$, $[styrene]_0 = 0.05M$. [b] Recovered styrene in mol %.

* Expt. 22 arbitrarily chosen as standard. † Total yields of the products (2)—(7) vs. consumed styrene.

since the results show that incorporation of a hydroxy- rather than an acetoxy-group predominates, the presence of water or a hydroxy-group to attack a cationic intermediate generated during the reaction is necessary. A simple explanation for the results is that adventitious water is responsible for the formation of the glycol monoacetates. Control experiments show clearly the

unchanged under these conditions or with only minor amount of benzaldehyde (experiment 14).

Two pathways are possible for the formation of (6); (1) a nucleophilic addition of acetate ion to a cationic intermediate, and path (2) acetylation of compounds (4) and (5). The lower yield of compound (6) in experiment 1 (as compared with experiment 12) and the small effect

TABLE 5

Effect of alkali acetates on product distribution [a]

Expt. no.	Temp. (°C)	Time (h)	Additives Ac₂O	Acetates	(1) [b]	(2)	(3)	(4) + (5)	(6)	(7)	(9)	(10)
30	60	70			20	5.6	4.5	25	6.1	6.6	Trace	
31	60	70		Na 0.1M	23	6.6	3.4	20	5.9	7.6	Trace	
32	60	70		K 0.05M	26	7.9	3.0	16	5.8	11	Trace	
33	120	18	5%		1.4	12	3.5		23	*	9.1	16
34	120	18	5%	Na 0.5M	9.5	7.8	1.1		16	*	7.4	9.2
35	120	18	5%	K 0.5M	9.4	13	0.8		14	*	7.8	10
36 [c]	120	13	5%	Na 1.0M	19	6.0	1.4		4.5	*	9.2	15
37 [c]	120	13	5%	K 1.0M	19	4.3	1.2		4.9	*	7.4	15
38 [d]	135	18	5%	K 3.0M	24	3.7	Trace		6.1	*	4.0	23

[a] Under N_2, $[Co^{III}]_0 = 0.10M$, $[styrene]_0 = 0.05M$. [b] Recovered styrene in mol %. [c] $[Co^{III}]_0 = 0.22M$, $[styrene]_0 = 0.10M$.
[d] $[Co^{III}]_0 = 0.20M$, $[styrene]_0 = 0.10M$.

* Exact yield was unknown because of contamination of benzoic acid.

contribution of water for the formation of (4) and (5) (experiments 23—25). Pretreatment of the solvent with acetic anhydride to remove water also resulted in a decreased yield of the glycol monoacetates as expected (experiments 26—29). However, not only the diacetate (6) but also compounds (2), (3), and (7), which are considered to be derived from the glycol monoacetates, were

of added acetate ion (experiments 31 and 32) reduces the possibility of path (1). Slow esterification of the glycol monoacetates must, therefore, in the main be responsible for the formation of (6).

It is found that the behaviour of cobalt(III) acetate shows some resemblance to that of lead(IV) acetate except that the latter oxidant with unsymmetrical

olefins [4,5] gives predominantly products resulting from skeletal rearrangement. The key to this rearrangement is the formation of a free carbocation (step 3 in Scheme 1). Thus the rearrangement competes with the incorporation of a nucleophile in the subsequent step: the former path sometimes predominates, especially if a potentially more stable carbocation can be formed thereby.

Unlike Pb^{IV} oxidations, the present results provide no evidence for the formation of the rearrangement product, 2-phenylethane-1,1-diol diacetate. The reaction of α-methylstyrene, which is expected to be a highly re-arrangement-prone system, with cobalt(III) acetate presented similar results in which rearrangement of the phenyl group scarcely occurred [under comparable conditions, optimum yields of the rearrangement products, benzyl methyl ketone and its acetate, PhCH(OAc)·COMe, were less than 1 and 2%, respectively].[1]

Even if the present reaction proceeds via such a stepwise mechanism as proposed for the Pb^{IV} oxidation
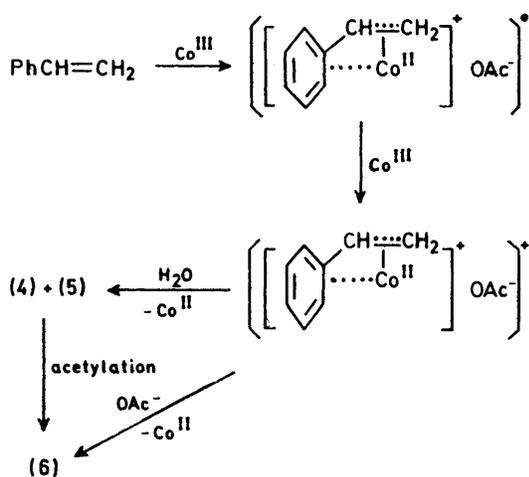
SCHEME 2

(Scheme 1), a lack of the rearrangement product indicates no formation of a ' free ' carbocation resulting from metal–carbon cleavage. Hence for the present reaction we propose a mechanism proceeding via an electron-transfer step (see 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 to a cation and subsequent addition of a nucleophile to the latter to yield a 1,2-addition product. There is evidence that the phenyl group contributes towards a stabilization of the intermediate, and an explanation for this has been reported.[1]

Formation of Radical Products.—In the dry system, rapid reduction of Co^{III} was observed as judged from the remarkable colour change of the reaction solution from dark green (Co^{III}) to pink (Co^{II}) regardless of the presence or absence of styrene. In the presence of styrene, the yields of (9) and (10) should be a measure of the extent of a radical pathway, since they result from the reaction of styrene with methyl and carboxymethyl radicals

generated on the decomposition of cobalt(III) acetate and by the subsequent reaction of methyl radical with AcOH [equations (2) and (3): see later]. In acetic acid, however, (9) and (10) were scarcely obtained even in the higher temperature range (Table 3). The results suggest that little decomposition of Co^{III} occurs and also imply that the reaction is a process with high activation energy as compared to that of the reaction with styrene. Thus it should be noted that decomposition of Co^{III} occurs more readily in the dry system than in either acetic acid or in wet acetic acid. Oxidation by cobalt(III) salts has been carried out mostly in aqueous media or in acetic acid,[13-25] and such a solvent effect on the stability of Co^{III} as well as the contribution of a radical mechanism to the oxidation has not yet been investigated, although there has been some speculation.[15] An acceptable explanation as to why Co^{III} decomposes so readily in the dry system is that a new complex is formed by displacement of OH ligand by acetate ion.* The new complex so formed would be thermally less stable than the neutral complex, and thus it appears that electron-transfer from acetate ligand (self-decomposition) becomes comparable to that from styrene (ionic reaction).

Literature reports [15,21] suggest that cobalt(III) acetate in acetic acid could decompose in the manner illustrated in equations (2) and (3). A methyl radical could then

$$Co(OAc)_3 \longrightarrow \cdot CH_3 + CO_2 + Co(OAc)_2 \quad (2)$$

$$\cdot CH_3 + CH_3CO_2H \longrightarrow \cdot CH_2CO_2H + CH_4 \quad (3)$$
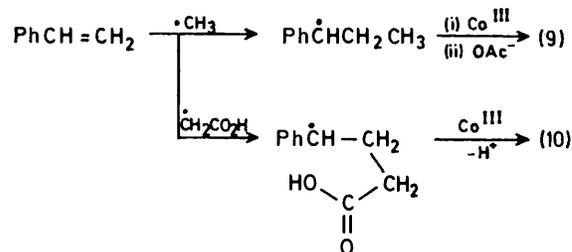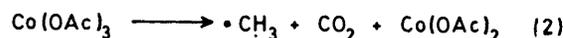
react either with styrene or with acetic acid; formation of a preponderance of γ-lactone relative to methyl adduct is considered to be a result of the difference in the concentrations of styrene and AcOH available for these reactions.

Manganese(III) acetate oxidation of olefins has been extensively studied, and most of the results have been successfully interpreted in terms of a radical mechanism. The reason why Mn^{III} behaves in such a different manner from the analogous one-electron oxidant, Co^{III}, remains a problem. However, direct comparisons of the mechanisms are not possible, since the Mn^{III} oxidations have been carried out mostly at higher temperature (reflux) and under rigorously dry conditions. Under these conditions, it has been found that a free-radical pathway is more favoured than an electron-transfer

* Cobalt(III) acetate is considered to be a di-μ-hydroxo-binuclear complex.[28,29]

one.[30] Hence it would be expected that a different mode of oxidation occurs under milder conditions as reported in a recent result.[25]

Summing up, the oxidation with cobalt(III) acetate proceeds *via* a mechanism similar to that proposed for Pb^{IV} oxidation except that oxidative rearrangement occurs extensively in the latter case. Lack of formation of a 'free' carbocation during the Co^{III} reaction and addition of a nucleophile to a Co co-ordinated intermediate offers a rational explanation for this unique behaviour. The finer details in the initial interaction of Co^{III} with the olefin still remain obscure although results have recently been reported.[24,25]

EXPERIMENTAL

^{1}H N.m.r. spectra were measured for solutions in carbon tetrachloride on a Japan Electron Optics Laboratory Co., Ltd. model JNM-C-HL spectrometer. Infrared spectra were determined for liquid films on a Japan Spectroscopic Co., Ltd. DS-403G spectrophotometer. Gas chromatography was carried out on a Shimadzu GC-4A instrument, with a 2 m column packed with PEG-20M 5% on Chromosorb GAW-DMCS, with temperature programmed from 70 to 170 °C at 4 °C min^{-1}. For measurement of yields, biphenyl was used as internal standard.

Starting Materials.—Styrene was commercial material and purified by distillation just before use. Cobalt(III) acetate was prepared either by peracetic acid oxidation [28] or by ozoniation [29] of cobalt(II) tetrahydrate in acetic acid containing acetic anhydride. The solution was evaporated to dryness under reduced pressure, and the solid obtained was stored in a desiccator. 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 more than 95%.

Oxidation Procedure.—A typical oxidation procedure was as follows. Styrene 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 flushed with dry nitrogen gas and sealed with a silicon-rubber stopper and then immersed in a thermostat. 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$_2$SO$_4$). Evaporation left a brown oil which was analysed by gas chromatography. The aqueous layer on acidification with hydrochloric acid gave a white precipitate which was recrystallized from water to give benzoic acid, m.p. 121 °C.

Identification of Products.—Reaction products, except for benzoic acid, were identified from their g.l.c. retention times. Benzylidene diacetate, 1-phenylethane-1,2-diol 1-acetate and 2-acetate, and 1-phenylethane-1,2-diol diacetate were also identified by isolating the samples by preparative g.l.c. and comparing their i.r., n.m.r., and mass spectra with those of the authentic samples.

Reference Compounds.—Benzaldehyde, benzylidene diacetate, and γ-phenylbutyrolactone were commercial materials. 1-Phenylpropyl acetate was prepared according to the literature.[31] A mixture of 1-phenylethane-1,2-diol 1-acetate and 2-acetate was obtained by Cohen's method.[27] 1-Phenylethane-1,2-diol diacetate was obtained by acetylation of the corresponding monoacetates with acetic anhydride.

REFERENCES

^{1} Part 1, M. Hirano and T. Morimoto, *J. Chem. Research,* 1979, (*S*) 104; (*M*) 1069.
^{2} H. J. Kabbe, *Annalen,* 1962, 204, 656.
^{3} A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I,* 1974, 1929.
^{4} R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B),* 1967, 771.
^{5} R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. (B),* 1968, 994.
^{6} Z. Rappoport, L. K. Dyall, S. Winstein, and W. G. Young, *Tetrahedron Letters,* 1970, 3483.
^{7} Z. Rappoport, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.,* 1970, 94, 2320.
^{8} R. J. Quellette, G. Kordosky, C. Levin, and S. Williams, *J. Org. Chem.,* 1969, 34, 4104.
^{9} M. Okano, *Bull. Chem. Soc. Japan,* 1976, 49, 1041.
^{10} W. J. de Klein, *Rec. Trav. chim.,* 1975, 94, 151.
^{11} E. I. Heiba, R. M. Dessau, and P. G. Rodewald, *J. Amer. Chem. Soc.,* 1974, 96, 7977.
^{12} E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.,* 1970, 92, 995.
^{13} C. E. H. Bawn, T. P. Hobin, and L. Raphael, *Proc. Roy. Soc.,* 1956, A237, 297.
^{14} F. Marta, E. Boga, and M. Matok, *Discuss. Faraday Soc.,* 1969, 46, 173.
^{15} R. Kawai and Y. Kamiya, *J. Chem. Soc. Japan,* 1973, 1533.
^{16} A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.,* 1973, 38, 3729.
^{17} A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.,* 1973, 38, 909.
^{18} K. Tanaka, M. Honda, and G. Inoue, *J. Chem. Soc. Japan, Ind. Chem. Sec.,* 1969, 72, 2587.
^{19} K. Tanaka, M. Honda, and G. Inoue, *J. Chem. Soc. Japan, Ind. Chem. Sec.,* 1969, 72, 2590.
^{20} Y. Kamiya and M. Kashima, *J. Catalysis,* 1972, 25, 326.
^{21} E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.,* 1969, 91, 6830.
^{22} T. Morimoto and Y. Ogata, *J. Chem. Soc. (B),* 1967, 1353.
^{23} Y. Kamiya and M. Kashima, *Bull. Chem. Soc. Japan,* 1973, 46, 905.
^{24} L. Verstraelen, M. Lalmand, A. J. Hubert, and P. Teyssie, *J.C.S. Perkin II,* 1976, 1285.
^{25} M. G. Vinogradov, Z. V. Todres, G. P. Il'ina, A. I. Rutavichus, D. N. Kursanov, and G. I. Nikishin, *Izvest. Akad. Nauk S.S.S.R. Ser. Khim.,* 1976, 1331.
^{26} R. M. Dessau, *J. Amer. Chem. Soc.,* 1970, 92, 6356.
^{27} T. Cohen, M. Dughi, V. A. Nataro, and G. Pinkus, *J. Org. Chem.,* 1962, 27, 814.
^{28} E. Koubek and J. O. Edwards, *J. Inorg. Nuclear Chem.,* 1963, 25, 1401.
^{29} S. S. Lande, C. D. Falk, and J. K. Kochi, *J. Inorg. Nuclear Chem.,* 1971, 33, 4101.
^{30} E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.,* 1969, 91, 138.
^{31} C. G. Overberger and D. Tanner, *J. Amer. Chem. Soc.,* 1955, 77, 369.