Allylic Oxidation of Olefins by Cobalt(III), Manganese(III), and Cerium(IV) Acetates in Acetic Acid in the Presence of Sodium Bromide

Takashi Morimoto,* Toshinori Machida, Masao Hirano, and Xiumin Zhung
Department of Industrial Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

The effect of added sodium bromide on the allylic oxidation of olefins by cobalt(III), manganese(III), and cerium(IV) acetates has been studied. Sodium bromide strongly accelerated the oxidation of cyclohexene by these oxidants to give cyclohex-2-enyl acetate in good yield. Only one product was obtained in the oxidation of cycloalkenes, but two allylic acetates were obtained in the oxidations of methyl-substituted cyclohexenes, which have two kinds of allylic hydrogen. A mechanism involving hydrogen abstraction from allylic sites by bromine radicals is suggested.

Many studies have been carried out on the allylic oxidation[1] of olefins by various metallic ions such as $\mathrm{Pb^{IV}}$,[2] $\mathrm{Hg^{II}}$,[2b,3] $\mathrm{Tl^{III}}$,[2d,4] $\mathrm{Pd^{II}}$,[5] $\mathrm{Se^{IV}}$,[6] $\mathrm{Cr^{VI}}$,[7] $\mathrm{Mn^{III}}$,[8] and some similarities in the behaviour of these oxidants towards olefins have been pointed out. However, none of these oxidants gives satisfactory yields and regioselectivity.

We have reported the allylic oxidation of some substituted olefins by cobalt(III) acetate in acetic acid to give selectively only one allylic acetate,[9,10] and have suggested the involvement of a cobalt-co-ordinated intermediate. In this paper, we report the effect of added bromide ion on yields and selectivities in the allylic oxidation of various olefins by cobalt(III), manganese(III), and cerium(IV) acetate in acetic acid. It has been reported that the oxidation of olefins[8] and toluenes[11] by manganese(III) is accelerated by the addition of potassium bromide, giving allylic or benzylic acetates, respectively, in good yields, but there is no detailed study reported on the selectivity of product formation and the mechanism.

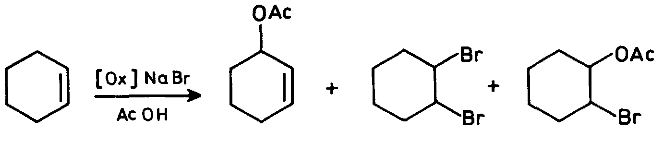
Results

When sodium bromide was added to a stirred mixture of cyclohexene (**1**) and cobalt(III) acetate in acetic acid, the dark green solution turned blue (pink on addition of water) in a few hours. G.l.c. analysis showed only two peaks, corresponding to recovered (**1**) and cyclohex-2-enyl acetate (**2**). The combined yield of these two compounds was close to 100% whenever an excess of olefin was used, showing that allylic oxidation was the only reaction occurring. Table 1 shows that 2—2.5 mol equiv. of cobalt(III) acetate were enough for complete oxidation of (**1**), giving a high yield of allylic acetate.

Sodium bromide is insoluble in acetic acid, but the salt gradually disappeared during the reaction and the mixture was homogeneous at the end unless a large excess of sodium bromide was used. Therefore the effects of bromide particle size, added water, and added acetic anhydride on the rate of reaction and yield of product were examined, but no marked influence was observed. Furthermore, stirring the reaction mixture had little effect. The slow dissolution of sodium bromide may be attributable to the formation of a cobalt(III) bromide species by ligand exchange.[12]

Various inorganic bromides were examined as promoters. All the bromides were effective, and sodium bromide was superior to the potassium and lithium salts. Thus, the sodium salt was employed in this study since it is also cheap and is easy to handle.

Cyclohexene was treated with various other oxidant–sodium bromide systems. The results are listed in Table 1, in which data for reactions in the absence of promoter are also given. Oxidation by cerium(IV) acetate gave only (**2**), in fairly good yield. That by manganese(III) acetate gave 1,2-dibromocyclohexane (**3**) and 2-bromocyclohexyl acetate (**4**) in addition to the main product (**2**). In this case, the yields of the former two products were higher at lower temperatures. On the other hand, the oxidations of the same olefin by copper(II) acetate and lead(IV) tetra-acetate in the presence of sodium bromide gave both (**3**) and (**4**), and only a trace of (**2**).



(**1**) (**2**) (**3**) (**4**)

Cyclohexene was treated with bromine in the presence and in the absence of cobalt(III), manganese(III), and cerium(IV) acetates. In all cases the reactions gave (**3**) and (**4**) in nearly 1:1 ratio, with trace of (**2**). The ratios of the former two products were almost independent of the presence or absence of the oxidants.

In order to elucidate the allylic oxidation, oxidations of 1-, 3-, and 4-methylcyclohexene were conducted in the presence of sodium bromide in acetic acid. In these cases, only allylic oxidation products were found (Table 2). When cobalt(III), manganese(III), or cerium(IV) acetate was used as oxidant in the presence of sodium bromide, 1-methylcyclohexene (**5**) was converted into 3-methylcyclohex-2-enyl acetate (**6**) and 6-methylcyclohex-2-enyl acetate (**7**) in 1:1 ratio; 3-methylcyclohexene (**8**) gave 4-methylcyclohex-2-enyl acetate (**9**) and the isomer (**6**) in 1:2 to 1:3 ratio (slightly changed by the reaction conditions); and 4-methylcyclohexene (**10**) gave 5-methylcyclohex-2-enyl acetate (**11**) and the isomer (**9**) in 1:1 ratio in moderate yields. The formation of four products from (**5**) and (**8**) and three from (**10**) was expected, but g.l.c. analysis showed that only two peaks corresponded to allylic acetates in every case. The one or two products missing in each case might be formed initially but undergo isomerisation to more stable acetates, but we have no evidence on this point. On the basis that isomerisation does occur, these results show that in the oxidation of (**5**) and (**10**), the two kinds of secondary allylic hydrogen are attacked at nearly equal rates, whereas in the case of (**8**) the tertiary hydrogen [finally giving (**6**)] is more rapidly abstracted than the secondary one [giving (**9**)].

A series of cyclic alkenes (**12**)—(**14**) and oct-1-ene (**15**) were treated with the cobalt(III) acetate–sodium bromide system which gave the optimum yield of allylic oxidation product. The results are summarised in Table 3. In all cases, allylic oxidation products were obtained in better yields under milder conditions

Table 1. Oxidation of cyclohexene by cobalt(III), manganese(III), and cerium(IV) acetates in the presence or absence of sodium bromide in acetic acid[a]

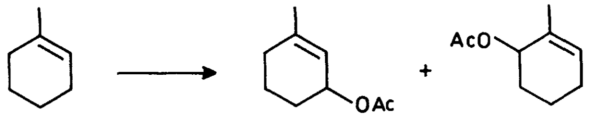
Oxidant	Temp. (K)	Time (h)	[NaBr]/[Olefin]	Recovered olefin (%)	Products (mol%) (2)	(3)	(4)
Co–NaBr	333	6	1.0	3	97	0	0
Co–NaBr	333	6	0.5	2	96	0	0
Co	333	24	0	4	57	0	0
Ce–NaBr	333	1	1.0	6	82	0	0
Ce–NaBr	353	1	1.0	2	79	0	0
Ce	333	24	0	54	6	0	0
Mn–NaBr	333	6	1.0	2	66	15	9
Mn–NaBr	333	0	0.5	3	66	9	6
Mn	333	24	0	70	1	0	0
Cu–NaBr	333	6	1.0	13	1	38	17
Cu–NaBr	353	6	1.0	14	2	24	15
Cu	333	24	0	79	0	0	0
Pb–NaBr	333	0.5	1.0	1	0	13	66
Pb–NaBr	333	1	1.0	1	0	14	76
Pb	333	24	0	11	24	0	0

[a] $[\text{Oxidant}]_0 = 2.02 \times 10^{-3}$ mol dm^{-3} in acetic acid; 5 cm^3 of the solution was used; $[\text{Oxidant}]_0/[\text{Olefin}]_0 = 2.5$.

Table 2. Product distributions for the oxidation of methylcyclohexenes by cobalt(III), manganese(III), and cerium(IV) acetates in acetic acid in the presence of sodium bromide[a]

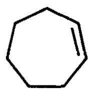
Olefin	Oxidant	Temp. (K)	Time (h)	[Oxidant]/[Olefin]	[NaBr]/[Olefin]	Products	Yield (mol %)	
(5)	Co^{III}	333	0.5	2.5	1.0	(6) + (7)	37	37
(5)	Co^{III}	313	24	5.0	0	(6) + (7)	59	1[b]
(5)	Ce^{IV}	283	0.13	2.5	1.0	(6) + (7)	27	22
(5)	Mn^{III}	333	1	2.5	1.0	(6) + (7)	22	24[c]
(8)	Co^{III}	303	0.5	2.5	1.0	(9) + (6)	14	28
(8)	Co^{III}	323	20	5.0	0	(9) + (6)	61	2[b]
(8)	Ce^{IV}	303	1	2.5	1.0	(9) + (6)	4	14
(8)	Mn^{III}	303	6	2.5	1.0	(9) + (6)	9	25[c]
(10)	Co^{III}	323	1	2.5	1.0	(11) + (9)	40	33
(10)	Co^{III}	323	24	5.0	0	(11) + (9)	50	0[b]

[a] Five cm^3 of oxidant in acetic acid ($[\text{Oxidant}]_0 = 2.02 \times 10^{-3}$ mol dm^{-3}) was used. [b] See also ref. 9*a*. [c] Some unidentified by-products were found.

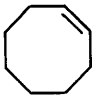


(5) **(6)** **(7)**

(12)



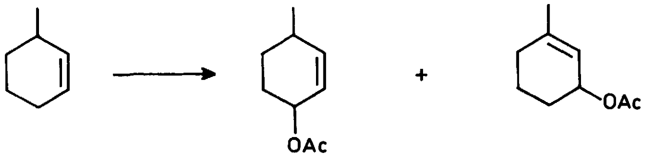
(13)



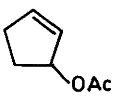
(14)

$C_5H_{11}CH_2CH=CH_2$

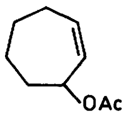
(15)



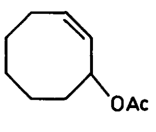
(8) **(9)** **(6)**



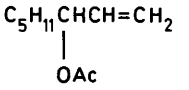
(16)



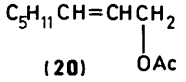
(17)



(18)

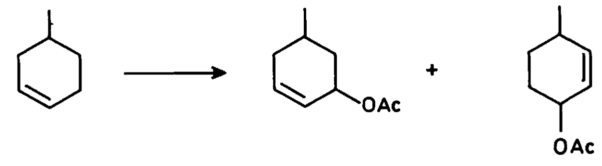


$\underset{\text{OAc}}{C_5H_{11}CHCH=CH_2}$



$C_5H_{11}CH=CH\underset{\text{OAc}}{CH_2}$

(20)



(10) **(11)** **(9)**

in the presence of bromide ion than in its absence. Only cycloalk-3-enyl acetates (16)—(18) were obtained in the oxidation of the cycloalkenes, although the yields of the products from five-, seven-, and eight-membered cycloalkenes were lower than that of cyclohexene, perhaps owing to the lower stability of the cyclopentane cation and to conformational effects in the cases of cycloheptene and cyclo-octene.[10] The oxidation of oct-1-ene (15) gave 3-acetoxyoct-1-ene (19) and 1-acetoxyoct-2-ene (20) in moderate yields in the ratio 1 : 1.

Table 3. Oxidation of cycloalkenes and oct-1-ene by cobalt(III) acetate[a]

Substrate	Temp. (K)	Time (h)	$\frac{[\mathrm{Co^{III}}]}{[\mathrm{Olefin}]}$	$\frac{[\mathrm{NaBr}]}{[\mathrm{Olefin}]}$	Recovered olefin (%)	Product(s)	Yield (mol %)	
(12)	323	2	2	0.5	*b*	**(16)**	20	
(12)	323	24	2.5	0	*b*	**(16)**	41	
(13)	333	6	2	0.5	5	**(17)**	54	
(13)	353	24	5	0	32	**(17)**	41	
(14)	333	4	2.5	1	20	**(18)**	54	
(14)	353	24	5.0	0	25	**(18)**	34	
(15)	353	48	2.5	1	32	**(19)** + **(20)**	32	33
(15)	353	48	2.5	0	75	**(19)** + **(20)**	6	7

[a] $[\mathrm{Co^{III}}]_0 = 2.02 \times 10^{-3}$ mol dm^{-3} in acetic acid; 5 cm^3 of the solution was used. [b] Not determined because of low b.p.

Discussion

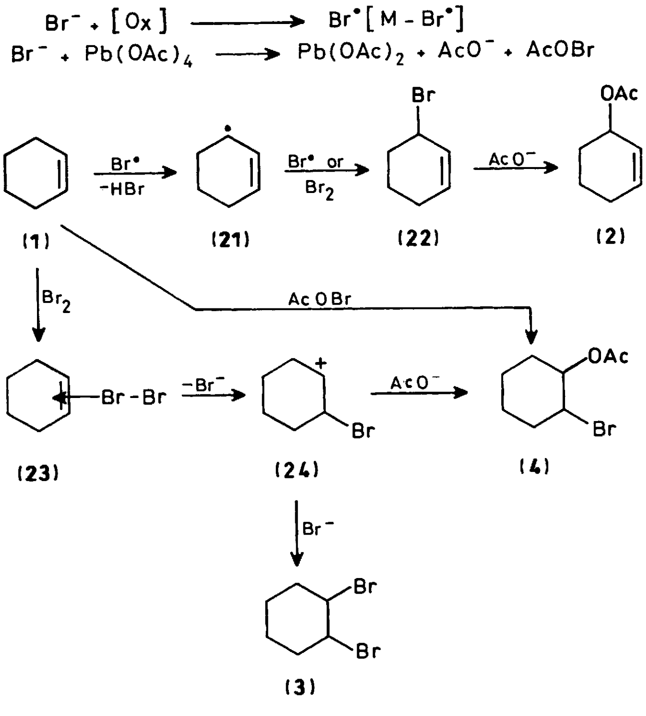
It is noteworthy that the products from the oxidation of cyclohexene with cobalt(III), manganese(III), and cerium(IV) acetates were markedly different from those with copper(II) and lead(IV) acetates. Dibromocyclohexane (**3**) and 2-bromocyclohexyl acetate (**4**) were obtained in oxidations by the latter two oxidants as well as in that by bromine in acetic acid, although there were some differences in the product ratios. These results show that the combination of sodium bromide with cobalt(III), manganese(III), or cerium(IV) produces a species which contributes to the allylic oxidation. There are literature reports on the promotion effect of sodium bromide on the azobisisobutyronitrile-initiated autoxidation of tetralin,[13] and on the cobalt(III) acetate-catalysed autoxidation of hydrocarbons,[12] where an intermediate radical or radical-like species plays an important role as a chain carrier. Thus, the species may be a bromine radical or a radical-like complex between a one-electron oxidant and bromide ion in the present reaction. This idea is supported by the fact that methyl-substituted cyclohexenes can be oxidized by these systems to give two kinds of allylic acetate, in product ratios similar to the relative sensitivities to hydrogen abstraction by bromine radicals.[14b]

Cobalt(III) acetate oxidation of methylcyclohexenes in the absence of sodium bromide gave regioselectively only one product; this was reasonably explained in terms of steric repulsion between the methyl group and the cobalt ligand in a cobalt-co-ordinated radical cation intermediate.[9] Manganese(III) and cerium(IV) acetates scarcely oxidized aliphatic olefins under the same conditions. These results may also imply the formation of active species other than metallic ions.

It is not difficult to understand why cobalt(III), manganese(III), and cerium(IV) acetate oxidations of olefins gave exclusively allylic acetates in acetic acid. These reagents are considered to be one-electron oxidants. Thus, transfer of one electron from bromide ion to the oxidant may afford a bromine radical, which may then co-ordinate to the reduced oxidant. The resulting species could abstract a hydrogen atom from the allylic position of the olefin to form an allylic radical.

The Scheme illustrates a possible reaction pathway following hydrogen abstraction by bromine radical or a bromine radical-like species.

Although no allylic bromide (**22**) could be detected by g.l.c. analysis, it is reported that organic bromides are principal products in the oxidation of toluenes and ketones by cobalt(III)[15] and manganese(III) acetate–sodium bromide systems[8,11] in acetic acid. Furthermore, 3-bromocyclohexene (**22**) was almost quantitatively converted into (**2**) in acetic acid containing cobalt(II) acetate and/or sodium bromide in 6 h at 333 K. These results show that a mechanism involving an organic bromide, formed through a radical chain reaction, is the most plausible.



Scheme.

On the other hand, lead(IV) and copper(II) acetates oxidize bromide ion to give molecular bromine without formation of a radical-like species. It is well known that molecular bromine adds to double bonds to form a bromine complex,[14] which then undergoes addition of acetate or bromide ion. Indeed the reaction of cyclohexene with molecular bromine gave both products, even in the presence of metallic salts. The same results have been reported in the oxidation of olefins by peracetic acid,[16] and confirmed in this study. The differences in product ratio of (**3**) to (**4**) may in part be attributable to solvolysis of these products, but the predominant formation of (**4**) in the lead(IV) acetate oxidation cannot be explained by this solvolysis alone. We found[14] that lead(IV) acetate can oxidize toluene to give ring-brominated compounds in the presence of sodium bromide, but copper(II) acetate cannot, showing that a powerful positive species is present in the former oxidation and not in the latter. Acetyl hypobromite has been suggested as an active species for the oxidation of olefins[16] and aromatic compounds[17] by peracetic acid. It may be the true active species in the present reactions.

There is another possible explanation of the allylic oxidation. It is well known that bromine in low concentration is an effective chain carrier for allylic reactions, as in bromination by *N*-bromosuccinimide.[14b] Thus, it is possible that bromine formed by oxidation of bromide ion is maintained at a low concentration in these systems, because of the poor solubility of sodium bromide in acetic acid. However, since bromine was observed in the reaction mixture when the substrate was absent, this mechanism may be negligible.

The present reaction is fast under mild conditions and gives few by-products. Thus, it may be a useful method of preparing allylic acetates, especially when only one allylic acetate can be obtained. The regioselectivity is unfortunately poor: several products can be obtained from methylcyclohexenes. In this case, cobalt(III)[9] and lead(IV)[2] acetates in the absence of bromide ion may be useful for selective allylic oxidation, although the reactions are slow.

Experimental

^{1}H N.m.r. spectra were measured for solutions in CCl_4 with a JEOL PMX-60 spectrometer. G.l.c. was carried out with a Shimadzu GC-6A instrument (2 m glass column packed with 5% PEG-20M on Chromosorb WAW-DMCS), with temperature programming. For measurements of yields, an internal standard was used. Preparative g.l.c. was performed with a Shimadzu GC-4A instrument (2 m stainless steel column packed with 30% PEG-20M on Celite 545) attached to a Shimadzu APP-5 fraction collector *via* a heated glass joint.

All reagents were commercially available and were used without further purification. Cobalt(III) acetate was prepared by bubbling ozone into acetic acid containing cobalt(II) acetate tetrahydrate and acetic anhydride.

Oxidation Procedures.—A typical procedure is as follows. In a round-bottomed flask, olefin and sodium bromide were mixed with cobalt(III) acetate in acetic acid. The vessel was then flushed with nitrogen, sealed with a glass stopper, and kept at a constant temperature in a thermostat with agitation. The solution was poured into water and the product was extracted three times with ether. The combined ethereal solution was washed successively with brine, aqueous 10% Na_2CO_3, and brine, and then dried (Na_2SO_4) and filtered. The ether was removed on a rotary evaporator to leave a pale-yellow oil, which was analysed by g.l.c. All the products were identified from comparison of their g.l.c. retention times and ^{1}H n.m.r. and i.r. spectra with those of authentic samples.[9a]

Several allylic acetates were available from the reactions of olefins with cobalt(III) acetate in the presence or absence of sodium bromide.

Cycloalk-2-enyl Acetate [**(2)**, **(16)**, **(17)**, *and* **(18)**].—The cycloalkene (*ca.* 3—3.5 g) was treated with cobalt(III) acetate in acetic acid (0.28—0.3 mol dm^{-3}; 500—700 cm^3) at 333 K for 24 h under nitrogen. After the same work-up as in the oxidation procedure, the products were distilled in a glass-tube oven: cyclopent-2-enyl acetate **(16)**; $\delta(CCl_4)$ 1.80—2.65 (4 H, m), 1.97 (3 H, s), and 5.33—6.18 (3 H, m); cyclohex-2-enyl acetate **(2)**; $\delta(CCl_4)$ 1.56—2.10 (6 H, m), 1.93 (3 H, s), 5.01—5.23 (1 H, m), and 5.57—5.89 (2 H, m); cyclohept-2-enyl acetate **(17)**; $\delta(CCl_4)$ 1.50—2.23 (8 H, m), 1.97 (3 H, s), 5.13—5.43 (1 H, m), and 5.57—5.90 (2 H, m); cyclo-oct-2-enyl acetate **(18)**; $\delta(CCl_4)$ 1.37—2.40 (10 H, m), 1.97 (3 H, s), and 5.25—5.87 (3 H, m).

3-*Methylcyclohex*-2-*enyl Acetate* **(6)**.—This compound was obtained from **(5)** by the method just described and purified by preparative g.l.c.; $\delta(CCl_4)$ 1.47—2.13 (6 H, m), 1.67 (3 H, s), 1.97 (3 H, s), and 4.83—5.52 (2 H, m).

2-*Methylcyclohex*-2-*enyl Acetate* **(7)**.—1-Methylcyclohexene **(5)** (0.87 g) was treated with cobalt(III) acetate solution (0.227 mol dm^{-3}; 100 cm^3) in the presence of sodium bromide (0.93 g) at 333 K for 30 min under nitrogen. The same work-up gave a mixture of **(6)** and **(7)**. Compound **(7)** was separated by preparative g.l.c.; $\delta(CCl_4)$ 1.50—2.17 (9 H, m), 1.97 (3 H, s), 4.98—5.23 (1 H, m), and 5.47—5.73 (1 H, m).

4-*Methylcyclohex*-2-*enyl Acetate* **(9)**.—3-Methylcyclohexene **(8)** (0.9 g) was treated with cobalt(III) acetate (0.23 mol dm^{-3}; 100 cm^3) at 323 K for 20 h under nitrogen. The product was purified by preparative g.l.c.; $\delta(CCl_4)$ 0.80—2.28 (8 H, m), 1.97 (3 H, s), and 4.88—6.02 (3 H, m).

5-*Methylcyclohex*-2-*enyl Acetate* **(11)**.—This compound was obtained from **(10)** by the method described for **(9)**; $\delta(CCl_4)$ 0.83—2.10 (8 H, m), 1.96 (3 H, s), and 5.03—5.93 (3 H, m).

3-*Acetoxyoct*-1-*ene* **(19)**.—Acrylaldehyde was added to an ethereal solution of pentylmagnesium bromide and the solution was refluxed for 30 min. After hydrolysis by aqueous ammonium chloride, the organic layer was separated and dried (Na_2SO_4). The ether was removed and the product was purified by distillation.

The resulting alcohol was refluxed with potassium acetate and acetic anhydride for 2 h. The mixture was poured into water and extracted with ether. The extract was washed with aqueous 10% Na_2CO_3 and water, dried (Na_2SO_4), filtered, and evaporated. The remaining oil was distilled through a Vigreux column to give the ester **(19)**; $\delta(CCl_4)$ 0.83—1.03 (3 H, m), 1.13—1.58 (8 H, m), 1.97 (3 H, s), and 4.93—6.01 (4 H, m).

1-*Acetoxyoct*-2-*ene* **(20)**.—Oct-1-ene **(15)** (0.92 g) was oxidized with cobalt(III) acetate (0.22 mol dm^{-3}; 100 cm^3) in the presence of sodium bromide (0.95 g). Work-up as described for **(7)** gave a mixture of **(19)** and **(20)**. The latter was separated by preparative g.l.c.; $\delta(CCl_4)$ 0.73—1.05 (3 H, m), 1.13—1.51 (6 H, m), 1.87—2.16 (2 H, m), 2.01 (3 H, s), 4.50 (2 H, d), and 5.43—5.77 (2 H).

References

1 (*a*) R. A. Sheldon and J. K. Kochi, 'Metal-catalysed Oxidation of Organic Compounds,' Academic Press, New York, 1981, p. 289; (*b*) D. J. Rawlinson and G. Sosnovsky, *Synthesis*, 1973, 567.

2 (*a*) R. Cryiegee, 'Oxidation in Organic Chemistry,' Part A, ed. K. B. Wiberg, Academic Press, New York, 1965, p. 337; (*b*) K. B. Wiberg and S. D. Nielsen, *J. Org. Chem.*, 1964, **29**, 3353; (*c*) G. H. White, *J. Chem. Soc.*, 1961, 2232; (*d*) A. Lethbridge, R. O. C. Norman, C. B. Thomas, and W. J. E. Parr, *J. Chem. Soc., Perkin Trans. 1*, 1975, 231; (*e*) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, 1968, **90**, 2706.

3 (*a*) W. Treibs and H. Bast, *Justus Liebigs Ann. Chem.*, 1949, **561**, 165; (*b*) Z. Rappoport, P. D. Sleezer, S. Winstein, and W. G. Young, *Tetrahedron Lett.*, 1965, 3719; (*c*) Z. Rappoport, L. K. Dyall, S. Winstein, and W. G. Young, *ibid.*, 1970, 3483.

4 J. B. Lee and M. J. Price, *Tetrahedron*, 1964, **20**, 1017.

5 (*a*) W. Kithing, Z. Rappoport, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, 1966, **88**, 2054; (*b*) S. Wolfe and G. C. Campbell, *ibid.*, 1971, **93**, 1497.

6 (*a*) K. B. Wiberg, 'Oxidation in Organic Chemistry,' Part A, ed. K. B. Wiberg, Academic Press, New York, 1965, p. 105; (*b*) A. Guillemont, *Ann. Chim. (Paris)*, 1939, **11**, 143; (*c*) J. P. Schaefer, B. Harvath, and H. P. Klein, *J. Org. Chem.*, 1968, **33**, 2647.

7 (*a*) W. G. Dauben, M. Lober, and D. S. Fullerton, *J. Org. Chem.*, 1969, **34**, 3587; (*b*) F. C. Whitmore and G. W. Pedlow, Jr., *J. Am. Chem. Soc.*, 1941, **63**, 758.

8 J. R. Gilmore and J. M. Mellor, *J. Chem. Soc. C*, 1971, 2355.

9 (*a*) M. Hirano, K. Nakamura, and T. Morimoto, *J. Chem. Soc., Perkin Trans. 2*, 1981, 817; (*b*) M. Hirano and T. Morimoto, *ibid.*, 1985, 1105.

10 L. Verstraelen, M. Lalmand, A. J. Hubert, and P. Teyssie, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1285.

11 J. R. Gilmore, *Chem. Commun.*, 1970, 507.

12 Ref. 1*a*, p. 126.

13 Y. Kamiya, ACS Advances in Chemistry Series, 1968, no. 76, p. 193.

14 (*a*) E. S. Huyser and D. N. Demott, *Chem. Ind. (London)*, 1963, 1954; (*b*) W. A. Pryor, 'Free Radicals,' McGraw-Hill, New York, 1966, p. 195.

15 T. Morimoto and M. Hirano, unpublished data.

16 Y. Ogata and K. Aoki, *J. Org. Chem.*, 1966, **31**, 4181.

17 Y. Ogata, Y. Furuya, and K. Okano, *Bull. Chem. Soc. Jpn.*, 1964, **37**, 960.

Received 21*st July* 1987; *Paper* 7/1329