γ-Tetrahydropyranol-*2,3,4,5,6-d_5* (4-d_5). A solution of 3.90 g of 3-d_4 in 30 ml of anhydrous ether was slowly added to a suspension of 1.65 g of $LiAlD_4$ in 65 ml of ether. After 6 h, the excess deuteride was destroyed with 10% H_2SO_4; the organic phase was then separated and the aqueous phase was extracted with chloroform. The combined organic phases were washed with a $NaHCO_3$ solution and water and then dried over $MgSO_4$. The solvent was then stripped. About 2.68 g (70%) of alcohol was obtained.

The identity of the product was determined to be 4-d_5 through characterization by its tosylate derivative (see below).

γ-Tetrahydropyranol-*2,4,6-d_3* (4-d_3). Compound 4-d_3 was obtained from 3-d_2 by a procedure identical with that described above. The identity of the product was confirmed through the identification of its tosylate derivative (see below).

Tetrahydropyran-*2,3,4,4,5,6-d_6* (5-d_6). A solution of 1.73 g of alcohol 4-d_5 in 15 ml of anhydrous pyridine was added to a solution of 4.0 g of *p*-toluenesulfonyl chloride (freshly recrystallized from petroleum ether) in 20 ml of pyridine and left standing for 48 h at 0 °C. Water (40 ml) and 55 ml of ether were then added and the organic phase was isolated. The aqueous solution was then extracted five times with 30 ml of ether. The combined ethereal solution was then washed successively with 3 N HCl, a saturated solution of $NaHCO_3$, and water, after which it was dried over $MgSO_4$ and stripped of its ether. The product was recrystallized from absolute ethanol and 3.17 g (90%) of pure tosylate was obtained, mp 55–56 °C (lit.[5] 56 °C).

The pure tosylate was then dissolved in 15 ml of anhydrous tetrahydrofuran and added slowly to a suspension of 700 mg of $LiAlD_4$ in 25 ml of tetrahydrofuran. After 90 h of reflux, 15 ml of water and 10% H_2SO_4 were added to destroy the deuteride left. The solution was then extracted five times with 30 ml of pentane and the organic phase was washed with a solution of $NaHCO_3$ and water. After drying over $MgSO_4$, the solution was concentrated by controlled distillation to about 7 ml. The product (5-d_6) was then obtained pure by preparative VPC using column B at 55 °C. It possessed a retention time equal to that of nondeuterated tetrahydropyran.

The product was then characterized by its ^1H NMR spectrum in carbon disulfide (Figure 1) and its isotopic composition was determined from its mass spectrum at 6 eV: $d_8 = 2\%$, $d_7 = 14\%$, $d_6 = 64\%$, $d_5 = 16\%$, $d_4 = 3\%$.

Tetrahydropyran-*2,4,4,6-d_4* (5-d_4). Compound 5-d_4 was prepared from 4-d_3 by a procedure identical with that described above. Purification by VPC provided pure 5-d_4 which showed a retention time identical with that of 5-d_6 and a ^1H NMR spectrum in carbon disulfide in accord with its proposed structure (Figure 2).

Acknowledgment. We wish to acknowledge the technical assistance of Mr. Robert Mayer with the recording of the ^1H NMR spectra at low temperatures and we are grateful to the National Council of Canada for financial assistance.

Registry No.—**2**, 108-97-4; *syn*-**3**-d_2, 58241-27-3; *anti*-**3**-d_2, 58241-28-4; *syn*-**3**-d_4, 58267-59-7; *anti*-**3**-d_4, 58267-60-0; *syn*-**4**-d_3, 58241-29-5; *anti*-**4**-d_3, 58241-30-8; *syn*-**4**-d_5, 58241-31-9; *anti*-**4**-d_5, 58267-61-1; *syn*-**5**-d_4, 58241-32-0; *anti*-**5**-d_4, 58241-33-1; *syn*-**5**-d_6, 58267-62-2; *anti*-**5**-d_6, 58267-63-3; tetrahydropyran, 142-68-7.

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Expoxidation of Olefins with Molecular Oxygen in the Presence of Cobalt Complexes

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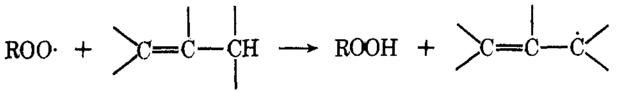
The epoxidation of *tert*-butylethylene, norbornylene, and 1,1-dineopentylethylene using molecular oxygen has been studied in the presence of cobalt(III) acetylacetonate. Epoxidations under these conditions show an induction period and other characteristics of a radical chain process, being inhibited by hydroquinone and promoted by azobisisobutyronitrile. A mechanistic scheme is presented in which the reaction between cobalt(III) acetylacetonate and oxygen initiates radical chain processes. β-Peroxyalkyl radicals are the key intermediates in the oxidation. Epoxide formation under these conditions bears a resemblance to the autoxidation of olefins studied by Mayo and co-workers. The olefins in this study were specifically chosen to preclude the formation of hydroperoxides. The results, thus, emphasize the caution which must be exercised in attributing the formation of epoxides solely to hydroperoxide intermediates in metal-catalyzed oxidations.

The oxidation of olefins catalyzed by transition metal complexes has become a subject of renewed interest, provoked by the desire to find evidence for the direct activation of molecular oxygen by metal complexes.[1-3] In most cases, however, the oxidation of the olefin can be traced to the presence of adventitious quantities of peroxidic impurities. For example, in 1967 Collman et al.[4] suggested the direct activation of molecular oxygen in order to explain the autoxidation of cyclohexene and cyclopentene by rhodium, iridium, and platinum complexes. A subsequent reexamination of the rhodium system[5] showed that hydroperoxides were involved. Indeed, a number of metal complexes including those of iron, cobalt, and rhodium catalytically decompose hydroperoxides via the redox processes represented in eq 1.[1,6]

$$RO_2H + M^n \longrightarrow RO\cdot + M^{n+1}(OH) \quad (1a)$$

$$RO_2H + M^{n+1} \longrightarrow RO_2\cdot + M^n + H^+ \quad (1b)$$

The resulting peroxy and oxy radicals usually initiate autoxidation by abstracting hydrogens from the olefin. The propagation steps, given in eq 2 and 3, lead primarily to products of allylic oxidation.



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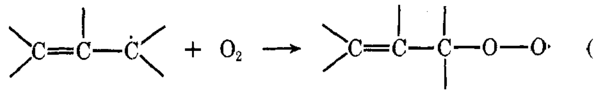
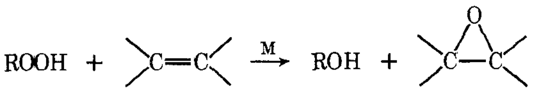


(3)

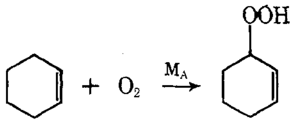
In 1973, Kaneda and co-workers[7] also reexamined the oxidation of cyclohexene with a rhodium catalyst.[7] They showed that the products of allylic oxidation resulted from reactions 1–3, but the formation of epoxide could not be accounted for by reactions proceeding via similar intermediates. Moreover, they ruled out a heterolytic process given in eq 4,[1,8] which is commonly observed for soluble metal complexes of vanadium, molybdenum, and tungsten.[8]



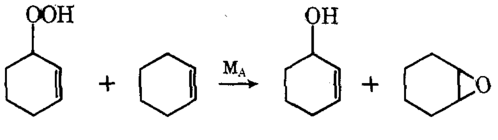
(4)

While the mechanism of the epoxide formation in Kaneda's studies has not been determined, it is clear that hydroperoxides are not directly involved. Although this system has been studied for the past 8 years, no satisfactory mechanism for epoxide formation has yet been demonstrated. In another example showing similar behavior, the autoxidation of cyclohexene in the presence of cobalt complexes gives oxidation products mainly from the reactions represented by eq 1–3.[6]

Recently, mixed catalyst systems have been used to give improved yields of epoxides in the autoxidation of cyclohexene.[9,10] One metal complex (M_A) is thought to catalyze the formation of hydroperoxide in eq 5a, while the second metal complex (M_B) is involved in the catalytic formation of epoxides according to eq 5b.



(5a)



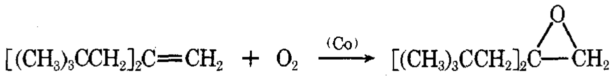
(5b)

The sequence of reactions given in eq 5a and 5b requires the ratio of epoxide to allylic alcohol to be less than or equal to unity. However, for a variety of mixed catalysts including cobalt complexes, ratios of epoxide/alcohol which are greater than unity have been observed. Thus, all of the epoxide cannot be explained as simply arising from the catalytic decomposition presented in eq 5b.

In the systems described above, olefin oxidations occur by at least two routes, one of which involves hydroperoxidic intermediates and the other which does not. With the most commonly used olefins such as cyclohexene, the facile reactions involving hydroperoxidic intermediates effectively mask the alternative routes for oxidation and make the study of the latter extremely difficult. With this complication in mind, we examined the reaction of cobalt acetylacetonate with olefins which do not easily undergo allylic oxidation in order to eliminate the ambiguities caused by hydroperoxides. Our results show that cobalt complexes can react with oxygen by homolytic pathways to convert olefins into epoxides. These processes do not involve hydroperoxides as such. Epoxide formation under our conditions bears a resemblance to the radical chain autoxidation of olefins previously delineated by Mayo and co-workers in the absence of metal complexes. The purpose of presenting our results here is to stress the participation of alternative routes for epoxide formation which do not involve hydroperoxidic intermediates when autoxidation of olefins are carried out in the presence of cobalt complexes. We have not attempted to elaborate on the earlier mechanistic studies of olefin autoxidation.

Results

The reaction of cobalt(III) acetylacetonate (1.0 mmol) with an excess of 1,1-dineopentylethylene[11] (25 mmol) in benzene (25 ml) under 10 atm of oxygen at 77 °C gave 0.95 mmol of 1,1-dineopentylethylene oxide after 17 h.

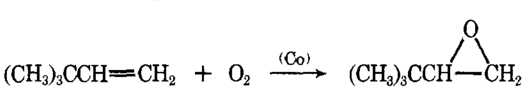


$$[(CH_3)_3CCH_2]_2C{=}CH_2 + O_2 \xrightarrow{(Co)} [(CH_3)_3CCH_2]_2C\overset{O}{-}CH_2$$

1 2

No reaction was observed in the absence of either oxygen or the metal complex. Under similar conditions cobalt(II) acetate tetrahydrate and cobalt(II) acetylacetonate gave 2 in yields of 0.95 and 0.10 equiv, respectively. No products of allylic oxidation or other volatile materials were found. Furthermore, no hydroperoxides were detected by iodometric titration.[12] Oxymolybdenum(VI) acetylacetonate, sodium acetate, or acetylacetone failed to give any olefin oxidation under the same conditions.

Reactions of *tert*-butylethylene (125 mmol) with cobalt(III) acetylacetonate (1 mmol) at 80 °C did not afford *tert*-butylethylene oxide. However, raising the temperature to 95 °C produced 1.70 mmol of the epoxide in 36 h. Under the latter conditions, iron(III) acetylacetonate afforded only 0.06 mmol of epoxide 4.



$$(CH_3)_3CCH{=}CH_2 + O_2 \xrightarrow{(Co)} (CH_3)_3CCH\overset{O}{-}CH_2$$

3 4

In addition to *tert*-butylethylene oxide, substantial amounts of acetone (0.77 mmol) and *tert*-butyl alcohol (0.81 mmol) were also formed during the oxidation employing cobalt(III) acetylacetonate. Iodometric titration detected no hydroperoxides when oxidations were carried out in the absence of the metal complex (even with added sodium acetylacetonate).

The conversion of olefin to oxidation products was very low for both dineopentyl- and *tert*-butylethylenes. On the contrary, norbornylene was easily oxidized in the presence of cobalt(III). Reaction of a benzene solution of norbornylene (56 mmol) with oxygen in the presence of cobalt(III)

Table I. Effect of Temperature on the Oxidation of Olefins[a]

Olefin	Temp, °C	Epoxide, mmol	CO_2, mmol
1[b]	60	0	*f*
1[b]	80	0.9[d]	*f*
1[b]	85	1.1[d]	*f*
1[b]	90	5.0[d]	*f*
1[c]	80	0.7[e]	1.4
1[c]	95	2.8[e]	4.2
1[c]	107	3.4[e]	5.2
1[c]	130	2.7[e]	5.2

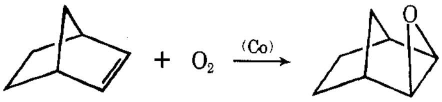
[a] Using 1.0 mmol of $Co(acac)_3$ in 25 ml of benzene; initial oxygen pressure 150 psi at 22 °C. [b] 1 = 1,1-dineopentylethylene, 25 mmol. [c] 2:1 mixture of 1,1-dineopentylethylene and 1-*tert*-butyl-2-neopentylpropene, 25 mmol. [d] Yield of 2 after 18 h. [e] Mixture of 2 and 1-*tert*-butyl-2-neopentylpropylene oxide after 18 h. [f] Not determined.

Table II. Effect of Oxygen Pressure on the Oxidation of Olefins[a]

Olefin[b]	O_2 pressure, psi	Epoxide,[c] mmol	CO_2,[d] mmol
1	0	0	0
1	15	0	0
1	100	0.50	0.8
1	150	0.65	1.4
1	200	0.60	1.3

[a] Using 1.0 mmol of $Co(acac)_3$ in 25 ml of benzene. [b] 2:1 mixture; see Table I, footnote *c*. [c] Yield of 2 after 18 h at 82 °C. [d] Yield after 18 h at 82 °C.

acetylacetonate (1 mmol) at 70 °C for 18 h resulted in greater than 95% conversion to oxidation products. *exo*-Norbornylene oxide (24 mmol, 43%) was the only volatile product obtained. The nonvolatile residue appears to be an oxygenated polymer containing less than 0.2% hydroperoxides by iodometric titration. A blank reaction carried out in the absence of the cobalt complex gave very low conversions (less than 1% epoxide) and less than 0.1% hydroperoxide by titration.



Effect of Temperature and Oxygen Pressure. To determine the range of reaction conditions over which epoxide formation occurred we varied the temperature and oxygen pressure. The effects of these changes upon epoxide formation from 1,1-dineopentylethylene in the presence of cobalt(III) acetylacetonate are shown in Tables I and II. The temperature studies were performed using both pure 1,1-dineopentylethylene and a mixture of triisobutylene isomers. The triisobutylene isomers were prepared by dehydration of *tert*-butyl alcohol in sulfuric acid[13] followed by treatment with alkaline permanganate solution.[11] The mixture of olefins consisted of 1,1-dineopentylethylene (64%) and 1-*tert*-butyl-2-neopentylpropene (36%) as determined by NMR spectroscopy. Oxidations using this olefinic mixture showed no significant amounts of the products of allylic oxidation or hydroperoxides. The composition of the mixture of epoxides was the same as that of the olefinic mixture used (see Experimental Section for details).

No oxidation of olefins was detected at or below 60 °C. The yields of epoxides reached a maximum at 107 °C. The lower yield of products observed at 130 °C were attributed to the subsequent decomposition of the epoxides at the high temperature, since control experiments showed that epoxides, which are stable at 90 °C, were decomposed to an extent of 33% after 19 h at 140 °C.

The effect of oxygen pressure was studied at 82 °C with cobalt(III) acetylacetonate using the mixture of triisobutylenes. No oxidation was observed when the oxygen atmosphere was replaced by argon (150 psi), or when low oxygen pressures (15 psi) were used.

The formation of carbon dioxide can also be used as a measure of the extent of reaction. Separately, the oxidation of a benzene solution of cobalt(III) acetylacetonate (1.0 mmol) in the absence of olefins at 130 °C produced 3.0 mmol of carbon dioxide. None of the cobalt(III) acetylacetonate could be recovered. In the absence of oxygen, no carbon dioxide was observed and most of the cobalt(III) acetylacetonate could be recovered after heating for 18 h at 130 °C. At 107 °C in the presence of the triisobutylene mixture all of the cobalt(III) complex was consumed, but at temperatures below 60 °C the cobalt(III) acetylacetonate was recovered unchanged after 18 h. Similarly at 82 °C under 1 atm of oxygen in the presence of dineopentylethylene no decomposition of the cobalt(III) acetylacetonate was detected. Under higher oxygen pressures (150 psi), increasing the temperatures resulted in increased cobalt(III) acetylacetonate decomposition. Monitoring the epoxide formation at 90 °C by GLC showed induction periods of greater than 6 h. When cobalt(III) acetylacetonate is consumed as described above, it changes from a green species soluble in benzene to an insoluble brown cobalt residue (presumably cobalt oxide since it no longer contains any organic components). This residue is an ineffective catalyst for the oxidation of olefins.

Effect of Additives. The effects of adding radical inhibitors and initiators are shown in Table III. The addition of free-radical traps such as hydroquinone severely retards the oxidation of olefins. Furthermore, radical initiators such as azobisisobutyronitrile (AIBN) increased the yields of epoxides without significantly changing the distribution of volatile products.

Oxidations Using Cobalt Carboxylates. Cobalt complexes in which acetylacetonato ligands have been replaced by various carboxylato ligands are also effective in promoting the oxidation of olefins as shown in Table IV. The change from the soluble cobalt(III) acetylacetonate to the much less soluble cobalt(II) species resulted in lower yields of epoxide. Some of the cobalt(II) is apparently converted to cobalt(III) under the reaction conditions as shown by the development of a green color during the reaction. The undissolved cobalt(II) compound can be recovered after the reaction. The addition of extra sodium acetylacetonate to the reaction had no effect upon the formation of epoxides. The more soluble cobalt(II) octoate gave epoxide yields comparable to those obtained with cobalt(III) acetylacetonate despite the presence of free carboxylic acid. Use of carboxylates such as pivalate and neodecanoate, however, gave significant increases in the yields of epoxides.

Discussion

Many of the previous studies[4,6,7,14] of olefin oxidation have employed cyclic alkenes such as cyclohexene which easily undergo allylic oxidation via reactions 1–3. Any less facile oxidation process can be masked by the more dominant autoxidation reaction. To avoid this problem we specifically chose olefins in which abstraction of an allylic hydrogen is disfavored relative to addition to the olefinic double bonds.[15,16] Thus, the autoxidation of norbornylene could be carried out to rather high conversions and reasonable yields of epoxide in the presence of cobalt complexes.

Table III. Effect of Additives on the Oxidation[a] of Olefins

Temp, °C	Olefin[b]	$Co(acac)_3$, mmol	Additive,[c] mmol	Epoxide, mmol	Acetone, mmol	t-BuOH, mmol
90	1	1.0		5.02[d]		
90	1	1.0	0.01 HQ	0.20[d]		
90	1	1.0	0.18 HQ	0.11[d]		
90	1	1.0	1.00 HQ	<0.05[d]		
95	3	1.0		1.70[e]	0.77	0.81
95	3	0	0.14 AIBN	1.30[e]	1.09	0.93
95	3	0	0.22 AIBN	2.12[e]	1.26	1.64
95	3	1.0	0.14 AIBN	4.10[e]	2.80	2.60

[a] Using 1.0 mmol of $Co(acac)_3$ in 25 ml of benzene for 18 h; initial O_2 pressure 150 psi. [b] **1** = 1,1-dineopentylethylene, 25 mmol; **3** = *tert*-butylethylene, 125 mmol. [c] HQ = hydroquinone; AIBN = azobisisobutyronitrile. [d] Epoxide **2**. [e] Epoxide **4**.

Table IV. Effect of Ligand Structure on Oxidation[a] of Olefins

Olefin[b]	Temp, °C	Metal complex,[c] mmol	Additive,[d] mmol	Epoxide, mmol	CO_2, mmol
3	95	1.0 $Co(acac)_3$		1.70[e]	h
3	95	1.0 $Co(acac)_2$		0.75[e]	2.20
3	95	1.0 $Co(acac)_2$	1.0 Na(acac)	0.72[e]	2.60
3	95	1.0 Co(II)oct	1.5 Hoct	1.36[e]	3.60
1	77	1.0 $Co(OAc)_2 \cdot 4H_2O$		0.95[f]	h
1*	80	1.0 $Co(acac)_3$		0.65[g]	1.40
1*	80	1.0 $Co(OAc)_3$		0.18[g]	0.10
1*	80	1.0 $Co(OAc)_3$	10.0 Na piv	2.14[g]	5.00
1*	80	1.2 Co(II) nd	0.8 Hnd	3.80[g]	3.60

[a] Reactions run in 25 ml of benzene for 18 h; initial O_2 pressure 150 psi at 22 °C. [b] **3** = *tert*-butylethylene, 125 mmol; **1** = dineopentylethylene; **1*** = 2:1 mixture of 1,1-dineopentylethylene and 1-*tert*-butyl-2-neopentylpropene, 25 mmol. [c] acac = acetylacetonate; OAc = acetate; oct = 2-ethylhexanoate; nd = 2,2-dimethyloctanoate. [d] Na piv = sodium pivalate. [e] Epoxide **4**. [f] Epoxide **2**. [g] Mixture of **2** and 1-*tert*-butyl-3-neopentylpropylene oxide. [h] Not determined.

Since small amounts of hydroperoxides were detected in the latter, we focused our attention in these studies on the less easily autoxidized *tert*-butylethylene and dineopentylethylene which showed no evidence of hydroperoxide formation.

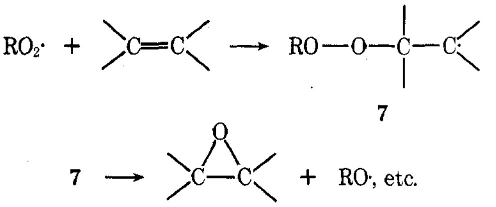
The results we have obtained from the oxidation of these olefins cannot be explained by either the allylic oxidation sequence in reactions 1–3 or by metal-catalyzed reaction between hydroperoxides and olefins described in reaction 4. The latter reaction can be dismissed for several reasons. First, it requires that at least equal amounts of alcohol and epoxide are formed. Second, no alcohol was formed in our reactions nor was any hydroperoxide detected. The substitution of molybdenum(VI) for cobalt(III) compounds resulted in no epoxide, although molybdenum complexes are known to catalyze the reaction between hydroperoxides and olefins.[5] Allylic oxidation can be ruled out by the absence of products of allylic oxidation and by the absence of hydroperoxides.

Our results are consistent with a direct reaction between oxygen and the metal complex. Thus, cobalt(III) acetylacetonate in benzene is stable in an inert atmosphere but it is decomposed in an oxygen atmosphere (150 psi) at 130 °C to produce ultimately carbon dioxide and a cobalt oxide. In the presence of olefins, oxidation occurs by a radical chain process, which shows long induction periods. Furthermore, radical inhibitors such as hydroquinone significantly retard the formation of epoxides and radical initiators such as AIBN increase the yields of epoxides. The close similarities between the product distributions obtained from the oxidation of *tert*-butylethylene using cobalt(III) acetylacetonate and the distribution obtained using AIBN suggests that similar propagation steps are involved in both systems.

Scheme I

Initiation: $Co(acac)_3 + O_2 \longrightarrow$ $Co(oxide) + CO_2 + R\cdot$ (6)

Propagation: $R\cdot + O_2 \longrightarrow RO_2\cdot$ (7)



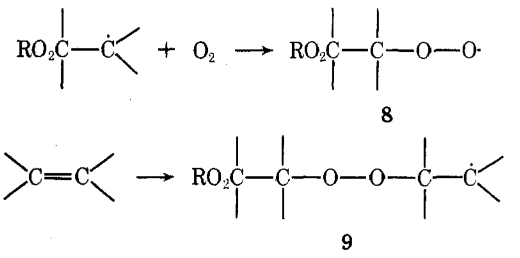
(8)

7

(9)

The oxidation of olefins which accompanies the reaction of oxygen with the cobalt complex can be explained by the sequence of reactions in Scheme I. According to this formulation, the cobalt complex serves as an initiator by producing free radicals during the reaction represented in eq 6. Peroxy radicals are readily formed by the subsequent reaction with oxygen. In the absence of any readily abstractable allylic hydrogens, addition to the ethylenic bond is favored to form the key intermediate **7**. Epoxides are known to result from the fragmentation in eq 9 of β-peroxyalkyl radicals such as **7**.[15]

The postulation of the β-peroxyalkyl radical **7** as an intermediate also allows the explanation of the other observations. Thus the competitive oxygenation of **7** in eq 10 produces the peroxy radical **8** which can add to another olefin in eq 11 forming the diperoxide radical **9**. In turn, **9** may

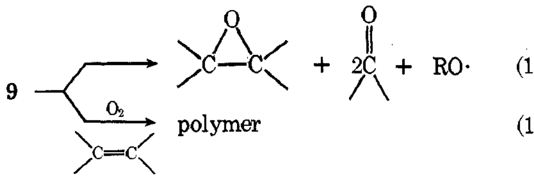


(10)

8

(11)

9



(12)

(13)

break down to epoxide and carbonyl compounds and generate an alkoxy radical (eq 12) or it may continue to react with more oxygen and olefin, ultimately producing oxygenated polymers.

The propagation sequence represented in Scheme I and in eq 10–13 is based on the studies of the autoxidation of olefins by Mayo and co-workers.[16] No doubt cobalt(II) and cobalt(III) species extant in the system are also capable of interacting with the alkyl, alkylperoxy, and alkoxy radical intermediates.[1,17] The extent to which these processes occur will certainly affect the distribution of the products of oxidation. Thus, the precise composition of the mixture of products will differ in the cobalt-induced autoxidation from that in the AIBN-initiated systems. All of these complex factors must be considered in any detailed study of the autoxidation of olefins.

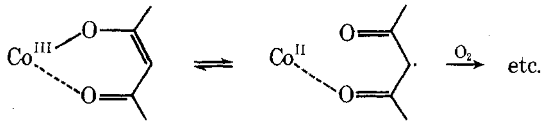
The mechanism by which cobalt complexes initiate the chain process involved in oxidation is not completely clear at this juncture. The formation of alkyl radicals during thermolysis of cobalt(III) carboxylates has been shown to lead to the radical chain decarboxylation of acids in the presence of oxygen, e.g.[18]

$$\mathrm{Co^{III}(O_2CR)_3 \longrightarrow Co^{II}(O_2CR)_2 + R\cdot + CO_2} \quad (14)$$

$$\mathrm{R\cdot + O_2 \longrightarrow RO_2\cdot \longrightarrow RO\cdot} \quad (15)$$

$$\mathrm{RO\cdot + Co^{II}(O_2CR)_2 + RCO_2H \longrightarrow ROH + Co^{III}(O_2CR)_3,\ etc.} \quad (16)$$

The ease of decarboxylation of acids follows the stability of the resulting radicals, i.e., tertiary > secondary > primary. Our results for cobalt carboxylates shown in Table IV can be interpreted on a similar basis. Thus, olefin oxidations in the presence of cobalt pivalate and neodecanoate, which form more stable tertiary alkyl radicals upon decomposition, gave higher yields of epoxides than oxidations promoted by cobalt acetate (which forms methyl radicals). Unlike the cobalt carboxylate complexes, a solution of cobalt(III) acetylacetonate in benzene is stable in an inert atmosphere. However, it is capable of initiating autoxidation of olefins at 80 °C in an oxygen atmosphere at pressures greater than 150 psi. Two explanations are possible. On one hand, cobalt(III) acetylacetonate may undergo a reductive fission analogous to that in reaction 14, except for its reversibility due to the bidentate nature of the acetylacetonato ligand. Reaction with oxygen could render the homolysis irreversible and lead to the initiation of radical chain processes. Alternatively, there may be a direct reaction between the cobalt center and molecular oxygen.[19] Indeed a wide variety of cobalt complexes, especially those of cobalt(II), are known to react with oxygen.[20] However, the chemistry associated with metal–peroxy radical species is largely undeveloped, especially with regard to the addition to olefins. Whereas the direct activation of molecular oxygen by cobalt cannot be ruled out for these systems, results on hand can be adequately explained by an initiation process in which radicals are formed during the reaction of soluble cobalt compounds with oxygen.



Experimental Section

Materials. Benzene, reagent grade, was distilled from a solution of sodium benzophenone ketyl and benzophenone dianion. It was passed over an alumina column prior to use. Triisobutylene was prepared following the method of McCubbin.[13] *tert*-Butylethylene was obtained from Sinclair Petrochemicals, Inc. Norbornylene was obtained from Aldrich Chemical Co., Inc. Pure 1,1-dineopentylethylene was obtained from triisobutylene following the method of Bartlett, Fraser, and Woodward.[11] All of the olefins were distilled from sodium, stored over sodium metal under nitrogen, and passed over an activated alumina column prior to use.

Authentic samples of epoxides were prepared from peracid oxidation of the appropriate olefins. An authentic sample of 1,1-dineopentylethylene oxide was prepared by treating dineopentylethylene with a 15% excess of *m*-chloroperbenzoic acid in methylene chloride at 0 °C for 2 h followed by 14 h at reflux (~40 °C). The solution was cooled to 0 °C and filtered to remove most of the *m*-chlorobenzoic acid. The filtrate was washed with 20% sodium bisulfite solution, 10% sodium bicarbonate solution, and finally with a saturated sodium chloride solution. The organic layer was dried over magnesium sulfate and filtered and the solvent removed in vacuo. The crude product was distilled in vacuo to give dineopentylethylene oxide, 72%: bp 49 °C (1 mm); NMR ($CDCl_3$) δ 2.62 (s, 2 H, oxirane ring hydrogens), 1.85 and 1.45 (coupled AB, $J = 16$ Hz, 4 H, methylene hydrogens), 1.00 (s, 18 H, methyl groups); low-resolution mass spectrum showed no molecular ion but gave m/e 169 ($M^+ - 15$), 113, 95, 85, 81, 72, 57, 43, 41, 29; ir (neat) 2960, 1470, 1250, 960, 820 cm^{-1}.

tert-Butylethylene oxide was prepared in 48% yield using the peracid procedure described above: bp 95°; NMR ($CDCl_3$) δ 2.65 (m, 3 H, oxirane ring protons), 2.65 (s, 9 H, *tert*-butyl group); mass spectrum again shows no parent ion at 100 but shows m/e 85 ($M^+ - 15$), 70, 55 as major fragments; ir spectrum shows no functional groups.

Norbornylene oxide[22] was prepared as above using the peracid oxidation of norbornylene. The crude product was sublimed at 85 °C: mp 118°; NMR (CCl_4) δ 2.90 (s, 2 H, $H_{1,2}$), 2.40 (s, 2 H, $H_{3,6}$), 1.0–1.6 (m, 5 H, H_4, H_5, H_{7syn}), 0.6 (m, 1 H, H_{7anti}); ir (CCl_4) epoxide bands at 1230 and 850 cm^{-1}.

A mixture of triisobutylene oxides was prepared according to the above procedure from triisobutylene.[13] The composition of the triisobutylene mixture used was determined by NMR integration based upon the following NMR assignments: 1,1-dineopentylethylene (CCl_4), 4.80 (s, 2 H, olefinic protons), 1.95 (s, 4 H, methylenes), 0.90 (s, 18 H, methyls of the neopentyl); 1-*tert*-butyl-2-neopentylpropene (CCl_4), 5.1 (s, 1 H, olefinic proton), 1.80 (m, 5 H, methylenes), 1.10 (s, 9 H, methyls of the *tert*-butyl group), 0.90 (s, 9 H, methyls of the neopentyl group). NMR integration showed a 2:1 mixture of the olefins, respectively. The composition of the epoxide mixture obtained after peracid oxidation of the olefin mixture was estimated by NMR integration to be 2:1 based upon the relative epoxide ring protons at δ 2.62 vs. 2.50. NMR of 2-*tert*-butyl-1-neopentylethylene oxide ($CDCl_3$): δ 2.50 (s, 1 H, ring proton), 1.45 (m, 5 H, allylic protons), 0.9–1.00 (m, 18 H, methyls of the neopentyl and *tert*-butyl groups, obscured by resonances from dineopentylethylene).

Metal acetylacetonates and carboxylates were obtained from the Shepherd Chemical Co. Sodium acetylacetonate and pivalate were obtained by neutralization of the protic species with sodium hydroxide. Cobalt(III) acetate was prepared by the ozonation of cobaltous acetate[21] obtained from Matheson Coleman and Bell. All other chemicals used were reagent grade.

Olefin Oxidation Reactions. Oxidations were carried out in a 300-cm Magnedrive Packless Autoclave using glass liners. In a typical run, the liner was charged with the cobalt complex (1.0 mmol), the olefin (either 25 or 125 mmol), and 25 ml of benzene. The autoclave was sealed and pressurized to 150 psi of oxygen at 22 °C. The gas was vented and repressurized twice to remove any air. The sealed autoclave was then heated to the desired temperature over a 1-h period with stirring rate of 1725 rpm. In some runs samples were periodically withdrawn through a sampling valve in order to monitor the reaction. At the end of the reaction, the contents of the autoclave were rapidly cooled to room temperature by passing cold water through the jacket.

Analysis of Products. The head gas was analyzed by venting a known portion of the noncondensible gases into an evacuated stoppered flask. Ethane was added as an internal standard and the mixture was analyzed for CO_2 on a 2-ft Porapak Q column carefully calibrated under the reaction conditions.

After venting the noncondensible gases the recovered solution was analyzed by gas–liquid chromatography. For reactions using *tert*-butylethylene, the volatile products (acetone, *tert*-butyl alcohol, and *tert*-butylethylene oxide) were analyzed on a 6-ft 15% FFAP column on Chromosorb P at 80 °C using methylcyclohexane as the internal standard. The products of the oxidation of norbornylene were analyzed on a 6-ft 15% TCEP column on Chromosorb W at 110 °C using *tert*-butylbenzene as the internal standard. The products of dineopentylethylene oxidation were analyzed using a 6-ft 15% TCEP column on Chromosorb W at 125 °C using *n*-tetradecane as the internal standard. GLC on a 6-ft SE-30 column at 200 °C showed that components boiling higher than the epoxides were not present.

A portion of the solution was titrated iodometrically for active oxygen following the procedure of Wibaut.[12]

The nonvolatile polymeric products were not analyzed in detail. Only the oxidation of norbornylene gave significant amounts of polymeric oxygenated products. The cobalt residues were separated from the solution by filtration, washed with organic solvents, and dried in vacuo. The volatile epoxides were separated by preparative GLC and identified by comparison of spectral properties with authentic samples prepared by peracid oxidation of the appropriate olefins.

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Registry No.—1, 141-70-8; 2, 4737-48-8; 3, 558-37-2; 4, 2245-30-9; *m*-chloroperbenzoic acid, 937-14-4; norbornylene oxide, 3146-39-2; norbornylene, 498-66-8; triisobutylene, 7756-94-7; 1-*tert*-butyl-2-neopentylpropene, 123-48-8; 2-*tert*-butyl-1-neopentylethylene oxide, 58191-06-3; 1-*tert*-butyl-2-neopentylpropylene oxide, 58191-07-4; Co(acac)$_3$, 21679-46-9; Co(acac)$_2$, 14020-48-7; Co(II)oct, 136-52-7; Co(OAc)$_2$, 71-48-7; Co(OAc)$_3$, 917-69-1; Co(II) nd, 32276-75-8.

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Copper-Catalyzed Oxidation of *o*-Phenylenediamines to *cis,cis*-Mucononitriles

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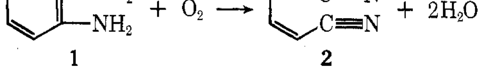
Oxidation of *o*-phenylenediamine (1) with molecular oxygen in the presence of CuCl in pyridine to give *cis,cis*-mucononitrile [(*Z,Z*)-2,4-hexadienedinitrile] was achieved in a high yield by selecting suitable reaction conditions. The molar ratio of 1 to CuCl in the reaction medium should be maintained below 0.5 in order to prevent intermolecular coupling of 1. *o*-Phenylenediamines substituted by electron-donating groups on the benzene ring gave the corresponding *cis,cis*-mucononitriles such as 3-methylmucononitrile, 3,4-dimethylmucononitrile, 3-methoxymucononitrile, and 3-chloromucononitrile, while no mucononitrile was obtained when electron-withdrawing groups were present. From 1,2-naphthalenediamine *o*-cyano-*cis*-cinnamonitrile was obtained. The structures of the products and the reaction mechanism are discussed.

Oxidation of organic compounds, especially phenols and aromatic amines, with molecular oxygen activated by metal salts is a well-established reaction. Oxidative coupling of aniline with oxygen catalyzed by CuCl gives azobenzene.[2] Also *o*-phenylenediamine (1) is oxidized in the presence of ferric chloride[3] to afford 2,3-diaminophenazine or 2-amino-3-oxophenazine in low yields. We have found that the oxidation of 1 can take a course completely different from the above ones by selecting proper reaction conditions; namely the ring cleavage reaction to give *cis,cis*-mucononitrile [(*Z,Z*)-2,4-hexadienedinitrile, 2] in a high yield proceeded smoothly at room temperature and under atmospheric pressure in the presence of CuCl in pyridine. Although 1



1 2

was oxidized to 2 by using a stoichiometric amount of nickel peroxide[4] or lead tetraacetate,[5] the yields were low and the metal salts cannot be reused. In contrast, the oxidation with CuCl gives an excellent yield of 2 and CuCl can be reused. This ring cleavage reaction resembles an enzymatic reaction of an oxygenase in regard to mild reaction conditions and participation of redox metals such as copper or iron.[6] The ring cleavage of pyrocatechol to *cis,cis*-muconic acid with pyrocatecase is a typical example.[7] A preliminary