

## Oxidation of Imines to Oxaziridines catalysed by Transition Metal Complexes using Molecular Oxygen as the Terminal Oxidant

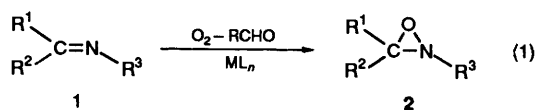
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The metal-catalysed oxidation of imines using molecular oxygen as the terminal oxidant and aldehydes as co-reductants has been studied. Different transition metal complexes have been tested as catalysts and it is found that cobalt complexes can catalyse the selective oxidation of imines to oxaziridines. The cobalt-catalysed oxidation of imines to oxaziridines is dependent on the aldehyde used as co-reductant; thus, the presence of aliphatic aldehydes leads to a smooth oxidation, whilst in the presence of aromatic aldehydes there was no reaction. The oxidation proceeds well for imines with aliphatic and aromatic substituents attached to the nitrogen and carbon atom, respectively. The electronic nature of the oxygen atom transferred in these reactions, investigated using thianthrene 5-oxide as a probe, was found to be electrophilic in character. The mechanistic aspects of the cobalt-catalysed oxidation of imines to oxaziridines, probably involving a peroxyacyl cobalt intermediate, are discussed.

A major goal in oxidation chemistry is to apply molecular oxygen ( $O_2$ ) as the terminal oxidant. Several bulk chemicals such as ethylene oxide<sup>1</sup> and maleic anhydride<sup>2</sup> are synthesised using a transition metal surface as the catalyst and  $O_2$  as the terminal oxidant. Until recently, only very few reactions have been available for the preparation of fine chemicals using the combination of a transition metal complex and  $O_2$ .<sup>3</sup> But, in recent years, several systems have been developed for the oxidation of organic compounds using  $O_2$  in combination with a transition metal complex and a co-reductant. By using this concept it has been possible to achieve both epoxidation<sup>4a-s</sup> and asymmetric epoxidation of alkenes,<sup>4j,m</sup> oxidation of alkanes<sup>4r,s,5</sup> and alcohols,<sup>4s,6</sup> Baeyer–Villiger oxidation of ketones<sup>4r,s,7</sup> and oxidative 1,4-addition to conjugated dienes<sup>8</sup> using mainly manganese-,<sup>4j,n</sup> cobalt,<sup>4i,o,n</sup> and nickel complexes<sup>4b-e,h,k,l,p,q</sup> as catalysts for the oxidations, while palladium complexes are applied as catalysts for the 1,4-additions.<sup>8</sup> The use of  $O_2$  as a terminal oxidant requires a co-reductant and mainly aldehydes are found useful for this purpose.<sup>4-7</sup>

The use of  $O_2$  as the terminal oxidant and a transition metal complex as the catalyst with an aldehyde as a co-reductant for the oxidation of organic nitrogen compounds has not, as far as we know, yet been achieved. This paper presents the first attempts to oxidise organic nitrogen compounds, especially the imines **1** by which the corresponding oxaziridines **2** are obtained, using this approach [reaction (1)].



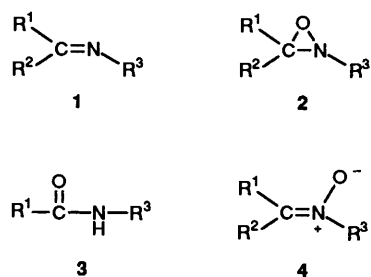
The oxaziridines **2**, a well-investigated class of compounds, are useful reagents in nitrogen- and oxygen-transfer reactions.<sup>9</sup> Oxaziridines have been employed industrially as nitrogen transfer reagents for the preparation of hydrazine derivatives,<sup>10</sup> while the *N*-sulfonyloxaziridines are applied as oxygen atom donors in synthetic organic chemistry.<sup>9,11</sup> Oxaziridines are obtained synthetically by two principal routes: one involves the reaction between a carbonyl compound and an amine derivative, carrying a suitable leaving group, giving the oxaziridine upon treatment with a strong base.<sup>9,12b,c</sup> The method most frequently employed is the reaction of a percarboxylic acid such as *m*-chloroperbenzoic acid (MCPBA) with an imine,<sup>9,11,12</sup> or a later improvement involving buffered,

easily available, potassium peroxymonosulfate (Oxone)<sup>13</sup> replacing MCPBA and thus avoiding a biphasic system.

Here we describe the development of a transition metal system as the catalyst for the oxidation of the imines **1** to the oxaziridines **2** using  $O_2$  as the terminal oxidant and a co-reductant, as well as, the synthetic and mechanistic aspects of this reaction.

### Results and Discussion

A series of transition metal complexes has been tested as catalysts for the oxidation of the imine **1a**. The reaction conditions for the test reactions were: **1a**:catalyst:co-reductant (2,2-dimethylpropanal) = 1:0.04:1 and an atmospheric pressure of  $O_2$  at 0 °C (for further details see Experimental section). The major product formed is the oxaziridine **2a**, besides some cleavage products. The results for the catalytic effect for different transition metal complexes are represented in Table 1.



- a  $R^1 = \text{Ph}$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{Bu}^t$
- b  $R^1 = p\text{-ClC}_6\text{H}_4$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{Bu}^t$
- c  $R^1 = p\text{-MeOC}_6\text{H}_4$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{Bu}^t$
- d  $R^1 = \text{Ph}$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{Bu}^t$
- e  $R^1 = \text{Ph}$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{Pr}$

The experiments in Table 1 show that of the five systems giving the oxaziridine **2a** (entries 3, 5–8), those containing  $\text{CoCl}_2$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Co}(\text{salicylaldehyde})_2$  were the most efficient (entries 5–7). The major by-products in these reactions were benzaldehyde and 2,2-dimethylpropanoic acid, but traces of the amide **3a** and/or the nitron **4a** were also occasionally observed. The benzaldehyde formed could arise from an over-oxidation, which would also form 2-methyl-2-nitropropane and/

**Table 1** Catalytic properties of various transition metal complexes in the oxidation of imine **1a** to oxaziridine **2a** using O<sub>2</sub> as the terminal oxidant<sup>a</sup>

Entry	Catalyst	Reaction time (h)	Conversion <b>1a</b> <sup>b</sup> (%)	Yield <sup>b</sup> <b>2a</b> (%)	Yield <sup>b</sup> PhC(O)H (%)
1	—	4.0	0	0	0
2	OV(acac) <sub>2</sub> <sup>c</sup>	2.0	2	0	9
3	Mn(salen)Cl <sup>d</sup>	2.0	46	47	53
4	FeCl <sub>3</sub>	2.0	18	Trace	18
5	CoCl <sub>2</sub>	2.0	100	77	23
6	CoCl <sub>2</sub> ·6H <sub>2</sub> O	3.5	100	74	26
7	Co(salicylaldehyde) <sub>2</sub>	1.0	48	70	30
8	NiCl <sub>2</sub> ·6H <sub>2</sub> O	6.7	46	23	77
9	Ni(salen) <sup>d</sup>	5.3	17	0	17
10	Ni(pc) <sup>e</sup>	2.0	13	0	13
11	Cu(OAc) <sub>2</sub> ·6H <sub>2</sub> O	5.5	16	0	16
12	Cu(salen) <sup>d</sup>	2.0	5	0	5
13	CuBr <sub>3</sub>	1.0	19	Trace	19

<sup>a</sup> Reaction conditions: **1a**:catalyst:2,2-dimethylpropanal = 1:0.04:1 and an atmospheric pressure of O<sub>2</sub> at 0 °C in CH<sub>2</sub>Cl<sub>2</sub>. Only the systems showing oxaziridine formation were continued for longer periods. <sup>b</sup> Yields and imine conversion are determined by <sup>1</sup>H NMR. In the reactions giving oxaziridine formation often a trace of the amide or nitron isomer was observed. <sup>c</sup> acac = acetylacetonate. <sup>d</sup> salen = *N,N*-bis-(salicylidene)ethylenediamine. <sup>e</sup> pc = phthalocyanine.

**Table 2** Oxidation of the imine **1a** to the oxaziridine **2a** using CoCl<sub>2</sub> as the catalyst and O<sub>2</sub> as the terminal oxidant in the presence of different aldehydes (RCHO) as co-reductant<sup>a</sup>

Entry	R	Equiv.	Reaction time (h)	Conversion <b>1a</b> <sup>b</sup> (%)	Yield <sup>b</sup> <b>2a</b> (%)	Yield <sup>b</sup> PhC(O)H (%)
1	Bu <sup>i</sup>	1	4.75	85	78	22
2	Pr	1	1	42	54	46
			2	43	36	64
3	Pr <sup>i</sup>	1	1	59	37	47
4	Pr <sup>i</sup>	1.2	1	69	64	36
5	Bu <sup>i</sup>	1	1	85	78	22
6	Bu <sup>i</sup>	1.2	1	100	78	22
7	Ph	1	0.75	0	0	0
8	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	1	4	0	0	0

<sup>a</sup> Reaction conditions: **1a**:CoCl<sub>2</sub>:aldehyde = 1:0.04:1/1.2 and an atmospheric pressure of O<sub>2</sub> at 0 °C in CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Determined by <sup>1</sup>H NMR.

or 2-methyl-2-nitrosopropane, or an acid-catalysed hydrolysis of **2a** which also could lead to the formation of *tert*-butylhydroxylamine (*vide infra*). The formation of **3a** and **4a** is probably due to rearrangement of **2a**, whereas the formation of 2,2-dimethylpropanoic acid is related to the role of 2,2-dimethylpropanal, as co-reductant (*vide infra*).

In the following, CoCl<sub>2</sub> has been chosen as the catalyst because it is both easily available and gives a slightly higher yield of **2a** compared with the other cobalt complexes. The role of the aldehyde in the oxidation of **1a** to **2a** has been tested under the following reaction conditions: **1a**:CoCl<sub>2</sub>:aldehyde = 1:0.04:variable at 0 °C and an atmospheric pressure of O<sub>2</sub>. The results are presented in Table 2.

These experiments show that the formation of **2a** takes place in all the cases where aliphatic aldehydes are the co-reductants (Table 2, entries 1–6), whereas no oxaziridine is formed when an aromatic aldehyde is employed (entries 7, 8). Of the aliphatic aldehydes tested 3-methylbutanal proved to be the most efficient giving 78% yield of **2a** at a conversion of 100% (entry 6). The percentage conversion of **1a**, and the yield of **2a**, are also dependent on the **1a**:aldehyde ratio and the reaction time. The conversion increases from 85 to 100% when the ratio of **1a**:aldehyde is changed from 1:1 (entry 5) to 1:1.2 (entry 6), whereas a prolonged reaction time causes a decomposition of the oxaziridine (entry 2). It was also observed that an imine:aldehyde ratio of 1:1.2 gives the highest yield of **2a**–**c** with **1a**–**c** as the substrate, whereas for imines with less steric hindrance at the nitrogen atom such as **1d**, **e**, an imine:aldehyde ratio of 1:3 is needed, to avoid incomplete conversion of the imine (*vide infra*). We are not, at present, able to account for this observation.

The CoCl<sub>2</sub>-catalysed imine to oxaziridine oxidation using O<sub>2</sub> as the terminal oxidant and an aldehyde as co-reductant also shows dependency on the temperature. Increased cleavage to give benzaldehyde was observed for room temperature reactions compared with those carried out at 0 °C. At temperatures < –20 °C the CoCl<sub>2</sub>–aldehyde coordination complex becomes insoluble in CH<sub>2</sub>Cl<sub>2</sub> and there is no reaction.

The formation of benzaldehyde in the reaction of **1a** may result from either over-oxidation or acidic decomposition. Since 2-methyl-2-nitrosopropane and 2-methyl-2-nitrosopropane have not been observed in these reactions, we conclude that benzaldehyde formation arises from acidic hydrolysis. In order to prevent this, we added base to neutralise the acid formed: three systems were tested. Addition of basic Al<sub>2</sub>O<sub>3</sub> to the reaction mixture gave a buffered biphasic system, but had no effect on the yield of **2a**. Pyridine, upon addition to the solution, gave immediate dissolution of the cobalt complex, but there was no further reaction. The CoCl<sub>2</sub>–pyridine complex so formed is probably inert as a result of pyridine being too strongly coordinated to the cobalt atom. Use of a biphasic system, sodium carbonate (2 equiv.) in CH<sub>2</sub>Cl<sub>2</sub>, gave an increase in the yield of **2a** to 90%. It should be noted, however, that the latter system works best if rigorously dry conditions are avoided.

After having optimised the oxidation conditions, we applied the system to a series of aliphatic and aromatic imines; only **1a**–**e** could, however, be oxidised to the corresponding oxaziridines **2a**–**e** (Table 3, entries 1–5). The by-products in these reactions are the corresponding aromatic aldehydes, 3-methylbutanoic acid and traces of the amide isomers **3a**–**e**. The variation in yield of **2a**–**e** can be accounted for by the imine reactivity and the stability of the oxaziridine. Imines with electron-donating

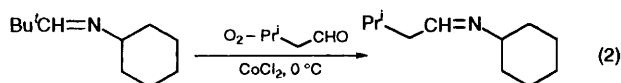
**Table 3** The oxidation of imines **1a–e** to the corresponding oxaziridines **2a–e** using  $\text{CoCl}_2$  as the catalyst and  $\text{O}_2$  as the terminal oxidant and 3-methylbutanal as co-reductant<sup>a</sup>

Entry	Imine	R <sup>1</sup>	R <sup>3</sup>	Reaction time (h)	2 <sup>b</sup> (%)
1	<b>1a</b>	Ph	Bu <sup>t</sup>	2.0 <sup>c</sup>	90
2	<b>1b</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Bu <sup>t</sup>	3.0 <sup>c</sup>	61
3	<b>1c</b>	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	Bu <sup>t</sup>	1.5 <sup>c</sup>	57
4	<b>1d</b>	Ph	Pr <sup>i</sup>	2.0 <sup>d</sup>	47
5	<b>1e</b>	Ph	Pr	2.0 <sup>d</sup>	48

<sup>a</sup> Reaction conditions: **1a–e**: $\text{CoCl}_2$ :3-methylbutanal = 1:0.04:1.2 or 3.0 and an atmospheric pressure of  $\text{O}_2$  at 0 °C in  $\text{CH}_2\text{Cl}_2$ . <sup>b</sup> Isolated yield. <sup>c</sup> 1.2 Equiv. of 3-methylbutanal. See general procedure A in Experimental section. <sup>d</sup> 3 Equiv. of 3-methylbutanal. See general procedure B in Experimental section.

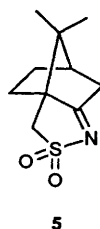
substituents are more easily oxidised to oxaziridines than those with electron-withdrawing substituents.<sup>12,14</sup> However, since the former are also known to be less stable than their electron-poor counterparts,<sup>12,14</sup> approximately equal yields of **2b** and **2c** were formed. Oxidation of imines with alkyl substituents at the nitrogen atom other than the *tert*-butyl group gave lower yields of the corresponding oxaziridine (entries 4, 5). The lower yields of **2d**, **e** agree with earlier observations that *N*-tertiary-alkyl-substituted oxaziridines are more stable than those with other *N*-alkyl substituents.<sup>12,14</sup>

The oxidation of imines other than those shown in Table 3 has also been attempted with  $\text{CoCl}_2$  as the catalyst,  $\text{O}_2$  as the terminal oxidant and 3-methylbutanal as co-reductant. Thus, we found that the imines **1** with R<sup>1</sup> = aryl, R<sup>2</sup> = alkyl and R<sup>3</sup> = alkyl/aryl or R<sup>1</sup> = alkyl, R<sup>2</sup> = hydrogen and R<sup>3</sup> = alkyl/aryl failed to give oxaziridines under either the present or modified reaction conditions; often, cleavage took place. Similarly, aliphatic imines failed to give significant yields of oxaziridines and, in some cases, cleavage of the imine to the aldehyde or exchange of the aldehyde part of the imine was observed [reaction (2)].

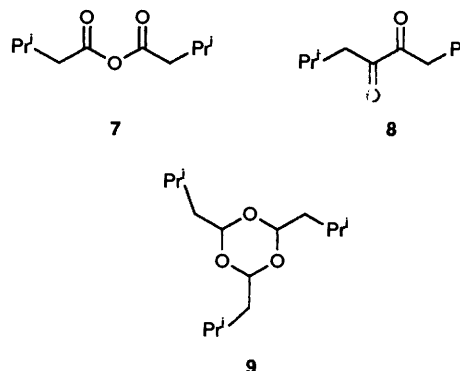


Further, since no 2-methyl-2-nitropropane and 2-methyl-2-nitrosopropane was formed it is possible that the aldehyde produced arises from acidic decomposition of the imine or maybe the oxaziridine. Our results for aliphatic imines agree with the known instability of both aliphatic imines, and, especially, aliphatic oxaziridines in the absence of stabilising electron-withdrawing groups.<sup>14</sup>

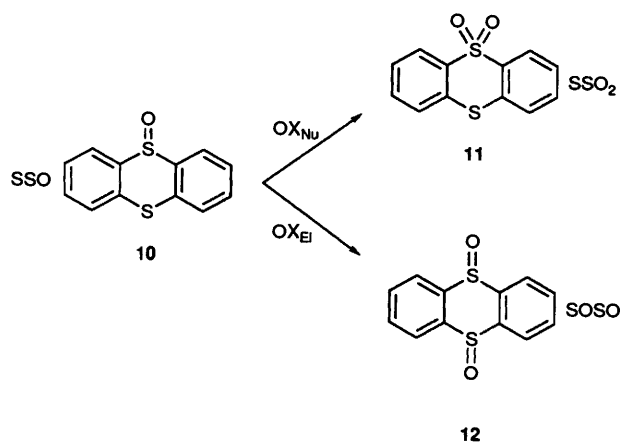
Attempted oxidation of the *S,S*-dioxide **5** and  $\text{PhCH}=\text{NSO}_2\text{Ph}$  **6** using  $\text{CoCl}_2$ ,  $\text{Co}(\text{salicylaldehyde})_2$  or  $\text{Mn}(\text{salen})\text{Cl}$  as the catalysts,  $\text{O}_2$  and 3-methylbutanal as co-reductant gave recovery of the former, and cleavage of the latter. Similar results were obtained for the attempted oxidation of 3,4-dihydroisoquinoline with  $\text{CoCl}_2\text{-O}_2$  and 3-methylbutanal both at 0 °C and at reflux in  $\text{CH}_2\text{Cl}_2$ .

**5**

An imine:aldehyde ratio of 1:3 is necessary for the reaction of imines with *N*-substituents other than *N-tert*-butyl group to ensure complete conversion of the imine; such conditions also gave an abnormal by-product, the NMR of which was very similar to that for 3-methylbutanal, except for the absence of the *CHO* resonance (9.74 ppm). Although the corresponding anhydride **7** (recently observed in the  $\text{CoCl}_2$ -catalysed reaction of aliphatic aldehydes with  $\text{O}_2$  in the absence of acetic anhydride<sup>15a</sup>) and 2,7-dimethyloctane-4,5-dione **8** (arising from coupling of two acyl radicals derived from 3-methylbutanal<sup>15a</sup>) were considered as possibilities for the identity of this by-product, both were discounted on the basis of spectroscopic and chemical evidence. The by-product is probably a trimer of 3-methylpropanal **9**, the condensation of which is known to be catalysed by Lewis or Brønsted acids and  $\text{Co}^{\text{II}}$  or  $\text{Co}^{\text{III}}$ .<sup>16</sup>



To investigate the electronic nature of the oxygen atom transferred in these cobalt-catalysed oxidations, thianthrene 5-oxide **10** was oxidised under reaction conditions similar to those employed for the oxidation of **1** to **2**. Of the two functional groups that can be oxidised in compound **10**, nucleophilic oxidants tend to oxidise the sulfoxide function to give **11** ( $\text{SSO}_2$ ), while electrophilic oxidants mainly oxidise the sulfide functionality leading to **12** ( $\text{SOSO}$ ).<sup>17</sup>



Scheme 1

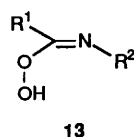
Adam has introduced the parameter  $X_{\text{SO}}$  defined as the  $\text{SSO}_2$  fraction of the total amount of oxidation products according to following equation:<sup>17</sup>

$$X_{\text{SO}} = \frac{n_{\text{SSO}_2}}{n_{\text{SSO}_2} + n_{\text{SOSO}}}$$

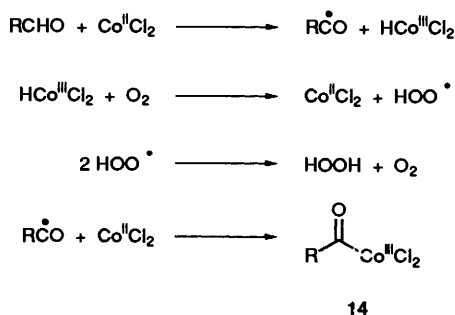
An  $X_{\text{SO}}$  value of 0, indicates an exclusively electrophilic oxidation, while an  $X_{\text{SO}}$  value of 1 is a nucleophilic oxidation. Since the oxidation of **10** using  $\text{CoCl}_2\text{-O}_2$  and 3-methylbutanal

as co-reductant gave an  $X_{SO}$  value of 0.1, the oxygen atom in this reaction is electrophilic in nature. It thus appears that the oxygen atom transferred in these cobalt-catalysed reactions is more electrophilic than the oxygen atom originating from MCPBA, which has a  $X_{SO}$  value of 0.36.<sup>17c</sup> The electrophilic nature of the oxygen atom generated in  $\text{CoCl}_2\text{-O}_2\text{-3-methylbutanal}$  reaction could account for our lack of success in attempting to oxidise compounds **5** and **6** to the corresponding oxaziridines, as the imine functionality in these substrates is very electron-poor in the presence of the sulfonyl group.

Several mechanisms for the cobalt-catalysed oxidation of the imines **1** to the oxaziridines **2** using  $\text{O}_2$  and an aldehyde as co-reductant can be envisaged. A peroxyimide intermediate **13** has been suggested in the autoxidation of imines.<sup>18</sup> Equal amounts of the oxaziridine **2** and the amide isomer **3** are formed when compound **1**, exposed to the air, is stirred at room temperature in the presence of traces of benzoyl peroxide.<sup>18</sup> Such results are explained in terms of the oxidation of **1** by  $\text{O}_2$  to give **13** which, in turn, oxidises a further molecule of **1** to give **2** and **3** in equal amounts.<sup>18</sup> Such a mechanism can be ruled out in the present reaction, since the presence of a cobalt catalyst leads only to traces of the amide isomer.



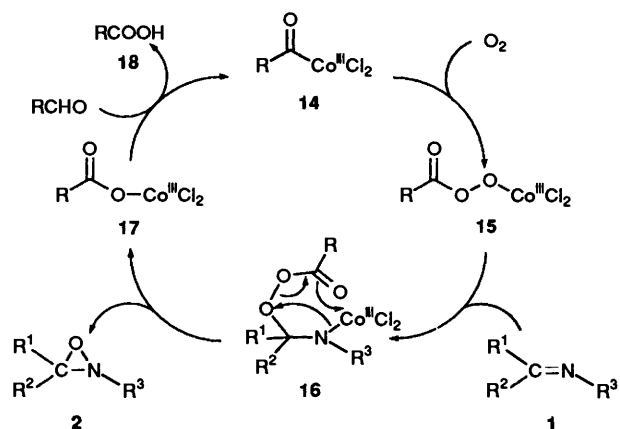
However, it is known that  $\text{CoCl}_2$  can react with aldehydes to give an acyl-cobalt complex,<sup>15a,19</sup> the generation of which is considered to be initiated by hydrogen abstraction from the aldehyde to generate a cobalt(III)-hydrido complex; this, upon reaction with  $\text{O}_2$ , regenerates  $\text{CoCl}_2$  and a hydroperoxide radical. The acyl-radical formed can then combine with  $\text{CoCl}_2$  generating the acyl-cobalt(III) complex, **14**.<sup>19</sup> The hydroperoxide radical formed may disproportionate spontaneously to give hydrogen peroxide and  $\text{O}_2$ .<sup>15a</sup> The formation of **14** is outlined in Scheme 2.



Scheme 2

Although the acyl-radical or **14** can be trapped with methyl acrylate,<sup>15</sup> in the absence of a radical trap  $\text{O}_2$  may be incorporated to form a acyl-peroxy-cobalt species **15**<sup>20</sup> (Scheme 3). Reaction of this with the imine **1** could give rise to a complex such as **16** leading, in turn, to the oxaziridine **2** and the cobalt carboxylate **17** (see in Scheme 3). The latter might then react with a further aldehyde molecule to form the corresponding acid **18**, regenerate **14** and complete the catalytic cycle.<sup>21</sup>

A mechanism involving the formation of a cobalt(III)-complex is suggested by the characteristic green colour of cobalt(III) complexes, observed only in successful reactions. Formation of such a species was also indicated when, in attempting to obtain an NMR spectrum at the beginning of the



Scheme 3

reaction course, we encountered difficulties because of the presence of a cobalt(II) complex having an unpaired electron and thus being paramagnetic. As the reaction proceeded, however, and after the green colour appeared, such difficulties disappeared, presumably because the  $\text{Co}^{\text{II}}$  species had been thereby converted into a  $\text{Co}^{\text{III}}$  complex. The  $X_{SO}$  value of 0.1 obtained for the  $\text{CoCl}_2\text{-O}_2\text{-3-methylbutanal}$  system suggests that the species responsible for the oxygen atom transfer is electrophilic in nature. On the basis of both experimental<sup>22</sup> and theoretical<sup>23</sup> evidence the oxidation of **1** to **2** by MCPBA is suggested to occur by nucleophilic attack of the peracid on the imine carbon atom followed by a rate-determining nucleophilic attack of the imine nitrogen atom on the electrophilic peroxy oxygen atom. A closely similar mechanism is proposed in the present work (see **16**), except that a cobalt(III) species acts as leaving group from the nitrogen atom and combines with the carboxylate group to give **17**.

As illustrated in Scheme 2 hydrogen peroxide may also be formed and act as an oxidant; in this case, an equimolar amount of water should have formed, as well as diones or other acyl-coupling products.<sup>15a,b</sup> Although water is indeed sometimes observed in these reactions, the absence of coupling products suggests that this mechanism is probably not operating. Finally, the presence of 3-methylbutanoic acid (isolated and identified by NMR and mass spectroscopy in all the successful reactions) supports the operation of a mechanism similar to that illustrated in Scheme 3.

Attempts to oxidise other nitrogen-containing compounds, such as secondary amines, using cobalt complexes and other transition metal complexes as catalysts, in combination with  $\text{O}_2$ , as the terminal oxidant and aldehydes as co-reductant, were unsuccessful.

In summary, we report here the first selective oxidation of imines to oxaziridines, in moderate to excellent yields, using  $\text{O}_2$  as the terminal oxidant. This is achieved by employing 4 mol%  $\text{CoCl}_2$  as catalyst and, usually, 3-methylbutanal as co-reductant. Although compounds with a variety of alkyl substituents on the nitrogen atom were employed, an aryl substituent on the imine carbon atom is necessary, to avoid cleavage of the aldehyde. Although the mechanism for the reactions is not yet fully established, it is thought to involve formation of an acyl-peroxy-cobalt species during the catalytic cycle.

## Experimental

**Materials.**—Solvents, metal complexes and aldehydes were those commercially available. Solvents were dried according to standard procedures before use. Aldehydes were purified prior

to use by standard methods. Anhydrous  $\text{CoCl}_2$  was obtained by drying the  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  at  $120^\circ\text{C}$  for 2 h. (7*S*)-(–)-10, 10-dimethyl-5-thia-4-azatricyclo[5.2.1.0]dec-3-ene 5,5-dioxide [(*S*)-camphor sulfonylimine] **5** was purchased from Aldrich Chemicals. The imines<sup>12a,24</sup> and thianthrene 5-oxide<sup>25</sup> were prepared according to literature. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 300 and 75 MHz, respectively. Chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  NMR are reported in ppm downfield from tetramethylsilane (TMS); *J* values are given in Hz. Mass spectra were recorded at 70 eV with a direct inlet. HPLC analysis was performed on a Nucleosil 10 CN column using *o*-nitroaniline as internal standard; eluent 10–25% propan-2-ol in cyclohexane.

**General Procedure A.**—The imine (0.5 mmol) was stirred with 3-methylbutanal (0.6 mmol, 1.2 equiv.) and  $\text{CoCl}_2$  (2.5 mg, 4 mol %) at  $0^\circ\text{C}$  under an atmosphere of  $\text{O}_2$  in  $\text{CH}_2\text{Cl}_2$  (5  $\text{cm}^3$ ). After the reaction time needed for complete conversion of the imine, the reaction mixture was filtered and evaporated and the oxaziridine isolated by column chromatography (**2a**, silica gel, 60 mesh,  $\text{CH}_2\text{Cl}_2$ ; **2b**, silica gel, 60 mesh, diethyl ether–light petroleum, 2:3; **2c**,  $\text{Al}_2\text{O}_3$ , 40 mesh, diethyl ether–light petroleum, 2:3).

**General Procedure B.**—The imine (0.5 mmol) was stirred with 3-methylbutanal (1.5 mmol, 3 equiv.) and  $\text{CoCl}_2$  (2.5 mg, 4 mol %) at  $0^\circ\text{C}$  under an atmosphere of  $\text{O}_2$  in  $\text{CH}_2\text{Cl}_2$  (5  $\text{cm}^3$ ). After the reaction time needed for complete conversion of the imine, the reaction mixture was filtered and evaporated and the oxaziridine isolated by column chromatography (silica gel, 60 mesh, diethyl ether–light petroleum, 2:3).

**2-tert-Butyl-3-phenyloxaziridine 2a**; colourless oil;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.36–7.46 (m, 5 H), 4.69 (s, 1 H) and 1.18 (s, 9 H);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 135.5, 129.7, 128.3, 127.5, 73.6, 58.4 and 25.2; *m/z* 177 ( $\text{M}^+$ ), 161, 146, 121, 105, 78 and 53.

**2-tert-Butyl-3-(*p*-methoxyphenyl)oxaziridine 2b**; colourless oil;  $\delta_{\text{H}}$  7.37 (d, 2 H, *J* 9.5), 6.90 (d, 2 H, *J* 9.5), 4.64 (s, 1 H), 3.81 (s, 3 H) and 1.17 (s, 9H);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 160.8, 128.9, 127.4, 113.8, 73.4, 58.2, 55.3 and 25.2; *m/z* 207 ( $\text{M}^+$ ), 191, 176, 151, 135, 108, 92, 77 and 53.

**2-tert-Butyl-3-(*p*-chlorophenyl)oxaziridine 2c**; white solid; mp 63–65  $^\circ\text{C}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.40–7.35 (m, 4 H), 4.66 (s, 1 H) and 1.17 (s, 9 H);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 135.6, 134.1, 128.9, 128.6, 72.9, 58.5 and 25.2; *m/z* 211 ( $\text{M}^+$ ), 195, 180, 155, 139, 111, 89, 75 and 53.

**2-Isopropyl-3-phenyloxaziridine 2d**; colourless oil;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.43–7.38 (m, 5 H), 4.51 (s, 1 H), 2.36 (heptet, 1 H, *J* 6.3), 1.33 (d, 3 H, *J* 6.3) and 1.18 (d, 3 H, *J* 6.3);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 135.1, 129.9, 128.5, 127.4, 80.1, 62.6, 21.3 and 18.9; *m/z* 163 ( $\text{M}^+$ ), 147, 132, 121, 105 and 77.

**3-Phenyl-2-propyloxaziridine 2e**; colourless oil;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.45–7.37 (m, 5 H), 4.49 (s, 1 H), 2.90–2.99 (dt, 1 H, *J* 12.1 and 7.4), 2.78–2.70 (dt, 1 H, *J* 12.1 and 7.4), 1.77 (sextet, 2 H, *J* 7.4), 1.03 (t, 3 H, *J* 7.4);  $\delta_{\text{C}}$  134.8, 130.0, 128.8, 127.5, 80.4, 63.9, 21.8 and 12.5; *m/z* 163 ( $\text{M}^+$ ), 146, 118, 105, 91 and 77.

**Thianthrene 5-Oxide Oxidation.**—Thianthrene 5-oxide (1.2 mmol) was stirred with 3-methylbutanal (1.2 mmol) and  $\text{CoCl}_2$  (2.5 mg, 1.7 mol %) in  $\text{CH}_2\text{Cl}_2$  (5  $\text{cm}^3$ ) under an atmosphere of  $\text{O}_2$ . HPLC after 1 and 2 h showed formation of thianthrene 5,10-dioxide (96%), thianthrene 5,5-dioxide (4%), starting material and a trace of the over-oxidized product thianthrene 5,5,10-trioxide.

Thianthrene 5-oxide **10**; white solid; mp 142–144  $^\circ\text{C}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.93 (dd, 2 H, *J* 7.6 and 1.4), 7.64 (dd, 2 H, *J* 7.6 and 1.1), 7.56 (td, 2 H, *J* 7.6 and 1.1) and 7.43 (td, 2 H, *J* 7.6 and 1.4);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 141.3, 129.8, 128.9, 128.3 and 124.4; *m/z* 232 ( $\text{M}^+$ ), 216, 203, 184, 171, 166, 152, 139 and 121.

Thianthrene 5,5-dioxide **11**; white solid; mp 167–169  $^\circ\text{C}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 8.19–8.23 (m, 2 H), 7.62–7.68 (m, 2 H) and 7.52–7.59

(m, 4 H);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 135.3, 135.1, 132.0, 128.7, 127.7 and 125.5; *m/z* 248 ( $\text{M}^+$ ), 200, 184, 171, 152 and 139.

Thianthrene 5,10-dioxide **12**; white solid; mp 280–282  $^\circ\text{C}$ ;  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 8.07 (dd, 4 H, *J* 5.6 and 3.1) and 7.73 (dd, 4 H, *J* 5.6 and 3.1);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 142.7, 131.3 and 127.6; *m/z* 248 ( $\text{M}^+$ ), 232, 216, 203, 200, 184, 171, 152 and 139.

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