A Facile Oxidation of Secondary Amines to Imines by Iodosobenzene or by a Terminal Oxidant and Manganese or Iron Porphyrins and Manganese Salen as the Catalysts

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The oxidation of secondary amines to imines by iodosobenzene or catalysed by either manganese(III) or iron(III) porphyrins, or by a manganese(III) salen complex with iodosobenzene as the oxygen donor has been investigated. Both aromatic and aliphatic amines can be oxidized smoothly to the corresponding imines with iodosobenzene as the oxidant and the elimination of hydrogen takes place towards the least substituted carbon. Manganese(III) and iron(III) porphyrins and manganese(III) salen are found to catalyse the oxidation of secondary amines to imines with iodosobenzene as the terminal oxidant. Those amines that are less reactive when iodosobenzene is the oxidant, can be converted to the imines in higher yields if a catalyst is added, compared with the uncatalysed reaction. By-products such as carbonyls and nitrones are found in some of these reactions. The manganese(III) salen complex is found to be the best catalyst, followed by manganese(III) porphyrin and iron(III) porphyrin. On the basis of Hammett plots, isotopic labelling studies and other experimental investigations the mechanisms for the uncatalysed and catalysed amine-to-imine oxidations are discussed.

The oxidation of amines, **1**, to the corresponding imines, **2**, [reaction (1)] can be achieved by various procedures, but the classical methods for this reaction are often limited and the final yields of the imines are usually low because the primary products tend to be oxidized further.[1] In recent years several methods have been developed for the oxidation of secondary amines to imines,[2] in which the oxidation reagent does not oxidize the imine further,[2] or the product imine is trapped as an α-cyanoamine.[2b] These amine-to-imine oxidation reagents have their limitations, as the substrate amine in most of the cases must be substituted with aromatic groups (R^1, R^2 and/or R^3 are aromatic groups in **1**). An exception to this has been reported by Barton *et al.*,[2b] who, by the use of phenylseleninic anhydride, have been able to oxidize dialkylamines to imines.

(1)

1 **2**

Catalytic oxidation of **1** to **2** has only been reported in a few cases: $RuCl_2(Ph_3P)_2$, with *tert*-butyl hydroperoxide as the oxygen donor, has been found particularly useful for the preparation of 1-azadienes and 3,4-dihydroisoquinolines.[3a] Oxidation of both primary and secondary amines catalysed by $RuCl_2(Ph_3P)_2$ with molecular oxygen or iodosobenzene as the oxygen donor has also been reported.[3b] Cobalt Schiff base complexes catalyse the oxidation of *N*-benzylanilines to the corresponding *N*-benzylideneanilines with molecular oxygen[3c] or *tert*-butyl hydroperoxide[3d,e] as oxygen donors.

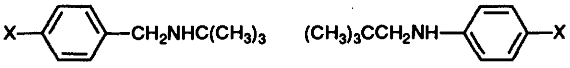
Iodosobenzene has been found useful as an oxygen donor in a variety of transition-metal-catalysed oxidations of different organic substrates including nitrogen compounds.[4] *N*,*N*-Dimethylbenzylamine has been found to undergo an oxidative demethylation to *N*-methylbenzylamine and debenzylation to benzaldehyde by iodosobenzene and *tert*-butyl hydroperoxide catalysed by iron(III) and manganese(III) porphyrins.[5] The present work will first focus on the oxidation of secondary amines to imines with iodosobenzene as the oxidation reagent. This procedure is successful for substrates containing aromatic substituents (R^1, R^2 and/or R^3 aromatic groups in **1**),† as well as for aliphatic amines (R^1, R^2 and R^3 aliphatic groups in **1**). A mechanistic investigation of the oxidation of **1** to **2** is presented. The effect on the reactivity of **1** of different substituents, including deuterium isotope effects, is reported. Secondly, the oxidation of the same amines catalysed by manganese(III) and iron(III) porphyrins or by manganese(III) salen with mainly iodosobenzene as the oxygen donor is reported. These reactions also give the corresponding imines as the major products.

Results and Discussion

Uncatalysed Oxidation of Amines, **1**, *to Imines,* **2**, *with Iodosobenzene as the Oxidation Reagent.*—A variety of secondary amines, **1a–j**, have been treated with iodosobenzene in CH_2Cl_2 at room temperature (see Experimental section). The results for the oxidation of the amines to imines are given in Table 1.

It appears from Table 1 that nearly all the amines are transformed into the corresponding imines in reasonable yields, with the exception of **1f** and **1j** (*vide infra*). It is also clear from Table 1 that the elimination of hydrogen from the amines seems to be Hofmann-like, as the double bond in **2i** is formed to the less substituted carbon atom rather than to the more substituted one. Furthermore, it should be observed that diisopropylamine, **1j**, is not oxidized under these reaction conditions.

In order to obtain further information about the mechanism of the amine-to-imine oxidation, oxidation of two series of



3a: X = H
3b: X = $N(CH_3)_2$
3c: X = OCH_3
3d: X = Cl
3e: X = NO_2

4a: X = H
4b: X = $N(CH_3)_2$
4c: X = OCH_3
4d: X = Cl
4e: X = NO_2

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† It should be noted that iodosobenzene has previously, in a few cases, been shown to oxidize aromatic amines to imines. See ref. 2*g*.

Table 1 Oxidation of secondary amines, **1**, to imines, **2**, by iodosobenzene in dichloromethane at room temperature[a]

	Substrates	Imine, **2**	Yield (%)[b]	Reaction time/h
1a	$PhCH_2NHC(CH_3)_3$	$PhCH{=}NC(CH_3)_3$	88	2
1b	$PhCH_2NHCH(CH_3)_2$	$PhCH{=}NCH(CH_3)_2$	78	2
1c	$PhCH_2NHCH_2CH_3$	$PhCH{=}NCH_2CH_3$	95	2
1d	$PhCH_2NHPh$	$PhCH{=}NPh$	31 (82)	2 (24)
1e	$PhCH_2NHCH_2Ph$	$PhCH{=}NCH_2Ph$	98	2
1f	$(CH_3)_3CCH_2NHPh$	$(CH_3)_3CCH{=}NPh$	16	46
1g	1,2,3,4-tetrahydroisoquinoline	3,4-dihydroisoquinoline	95	2
1h	$CH_3(CH_2)_3NH(CH_2)_3CH_3$	$CH_3(CH_2)_2CH{=}N(CH_2)_3CH_3$	82	2
1i	$CH_3(CH_2)_2NHC_6H_{11}$	$CH_3CH_2CH{=}NC_6H_{11}$	45	2
1j	$(CH_3)_2CHNHCH(CH_3)_2$	$(CH_3)_2C{=}NCH(CH_3)_2$	<2	76

[a] Amine, 0.1 mmol cm^{-3} and PhIO, 0.2 mmol cm^{-3}. [b] Yield based on the amine.

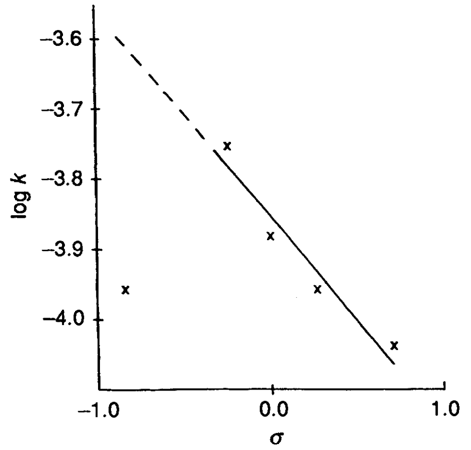


Fig. 1 Hammett plot for the reaction of **3a–e** with iodosobenzene

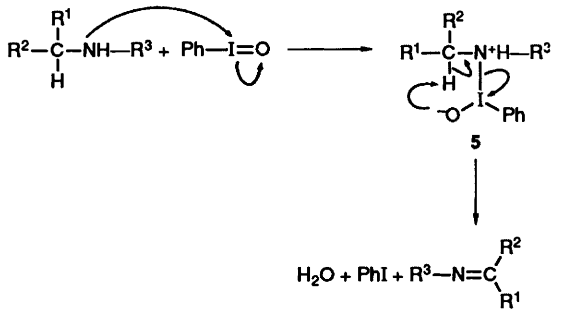
secondary *para*-substituted benzylamines, **3a–e**, and secondary *para*-substituted phenylamines, **4a–e**, has been carried out.

The oxidation of **3a–e** was studied at 20 °C under pseudo-first-order reaction conditions and the following rate constants were obtained: **3a**: $k = 8.8 \times 10^{-5}\ s^{-1}$; **3b**: $k = 7.3 \times 10^{-5}\ s^{-1}$; **3c**: $k = 11.6 \times 10^{-5}\ s^{-1}$; **3d**: $k = 7.5 \times 10^{-5}\ s^{-1}$ and **3e**: $k = 5.6 \times 10^{-5}\ s^{-1}$. No simple correlation between log k for the disappearance of **3a–e** and the Hammett substituents constants exists; the best correlation is found for σ in which **3b** is excluded from the correlation. It should also be noted that log k for the disappearance of **3a**, **c–e** correlates with neither σ^+ nor σ^-. The Hammett plot for the disappearance of **3a–e** is shown in Fig. 1.

The slope of a plot of log k for the disappearance for **3a**, **c–e** as a function of σ has been calculated to be -0.3 (correlation coefficient: 0.97). Fig. 1 indicates that log k for the disappearance of **3b** does not match the other results, which could indicate that the reaction of **3b** with iodosobenzene is different from the others (*vide infra*). Reaction of the substituted phenylamines **4a**, **c–e** with iodosobenzene is a slower reaction than that with **3a–e** as the substrate. The disappearance of these substrates at 20 °C under pseudo-first-order reaction conditions gives the following rate constants: **4a**: $k = 1.2 \times 10^{-5}\ s^{-1}$; **4c**: $k = 2.3 \times 10^{-5}\ s^{-1}$; **4d**: $k = 0.6 \times 10^{-5}\ s^{-1}$ and **4e**: $k = 0.05 \times 10^{-5}\ s^{-1}$. These results are found to correlate with σ, with a ρ value of -1.6 (correlation coefficient: 0.96), showing that the substituent in the *para* position of the phenyl group in **4** affects the reaction rate more than changes in the phenyl substituent in **3**.

The isotope effect for the reaction has also been studied; the reaction of $Ph{-}CH_2{-}NH{-}C(CH_3)_3$ and $Ph{-}CD_2{-}NH{-}C(CH_3)_3$ with iodosobenzene was found to exhibit no significant isotope effect (< 1.2), indicating that breaking of the C–H bond is not involved in the rate-determining step. It has been observed that the oxidation of **1a** to **2a** is not affected by radical traps, as the presence of $Ph{-}CH{=}N(O){-}C(CH_3)_3$ during the reaction leads to the same yield of **2a** under similar reaction conditions as is obtained without the presence of the radical trap.[6]

Based on the experimental results a mechanism as outlined in Scheme 1 for the reaction of secondary amines with iodosobenzene and formation of the corresponding imines has been proposed.*



Scheme 1

The first step in this mechanism is a nucleophilic attack by the nitrogen lone pair electrons of the amine at the iodine of iodosobenzene, leading to intermediate **5**. The negatively charged oxygen in **5** then attacks the most acidic α-proton, as outlined in Scheme 1, leading to the imine, iodobenzene and water. The rate-determining step is probably the first as using substituted phenyls R^1 or R^3 results in a negative ρ value indicating that electron density on the amine nitrogen is important. The variation in reaction rate is largest when changing R^3, as this substituent is nearer the reaction site. The deuterium labelling experiment also indicates that the first step in Scheme 1 is rate determining as no significant isotope effect is observed in the reaction. How can we then explain the observed slow reaction rate of **3b**, which according to the mechanism outlined in Scheme 1 and the discussion above, should be expected to be the fastest? We suggest that the reason for the unexpectedly slow reaction of **3b** with iodosobenzene is probably due to the *N*,*N*-dimethyl group; the nitrogen atom in the *N*,*N*-dimethyl group can also function as a nucleophile and attack the iodine in iodosobenzene, but does not lead to the desired reaction. It has also been observed that the yield of the expected imine is lower than anticipated, compared with the oxidation of the other amines.

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* See also ref. 2g.

Table 2 Oxidation of secondary amines, **1**, to imines, **2**, by iodosobenzene and various transition-metal catalyst complexes in dichloromethane[a]

Entry	Substrate	Imine	Catalyst	Yield (%)[b]	Reaction time/h (temp)	By-products (%)
1	**1a**	**2a**	—	31	2 (0 °C)	—
2	**1a**	**2a**	Fe^{III}(tpp)Cl	57	2 (0 °C)	PhCHO (24)
3	**1a**	**2a**	Mn^{III}(tpp)Cl	61	2 (0 °C)	PhCHO (25)
4	**1a**	**2a**	Mn^{III}(salen)Cl	80	2 (0 °C)	PhCHO (16)
5	**1d**	**2d**	—	10	2 (0 °C)	—
6	**1d**	**2d**	Fe^{III}(tpp)Cl	21	2 (0 °C)	PhCHO (8)
7	**1d**	**2d**	Mn^{III}(salen)Cl	52	2 (0 °C)	PhCHO (8)
8	**1e**	**2e**	—	98	2 (20 °C)	—
9	**1e**	**2e**	Fe^{III}(tpp)Cl	45	2 (0 °C)	PhCHO (9); PhCH=N(O)CH$_2$Ph (4)
10	**1f**	**2f**	—	16	46 (20 °C)	—
11	**1f**	**2f**	Fe^{III}(tpp)Cl	65	2 (0 °C)	(CH$_3$)$_3$CCOOH (9)
12	**1f**	**2f**	Mn^{III}(tpp)Cl	50	4 (0 °C)	(CH$_3$)$_3$CCOOH (20)
13	**1f**	**2f**	Mn^{III}(salen)Cl	54	4 (0 °C)	(CH$_3$)$_3$CCOOH (18)
14	**1j**	**2j**	—	<2	76 (20 °C)	—
15	**1j**	**2j**	Fe^{III}(tpp)Cl	15	2 (0 °C)	(CH$_3$)$_2$C=N(O)CH(CH$_3$)$_2$ (8)
16	**1j**	**2j**	Mn^{III}(tpp)Cl	70	2 (0 °C)	(CH$_3$)$_2$C=N(O)CH(CH$_3$)$_2$ (10)
17	**1j**	**2j**	Mn^{III}(salen)Cl	53	2 (0 °C)	(CH$_3$)$_2$C=N(O)CH(CH$_3$)$_2$ (31)

[a] Amine, 0.1 mmol cm^{-3}; PhIO, 0.2 mmol cm^{-3}; catalyst, 0.005 mmol cm^{-3}. [b] Yield based on the amine.

Oxidation of Amines, **1**, *to Imines,* **2**, *Catalysed by* Mn^{III}(tpp)Cl, Mn^{III}(salen)Cl *or* Fe^{III}(tpp)Cl *with Iodosobenzene or Sodium Hypochlorite as the Oxygen Donors.*—The oxidation of **1a–c** catalysed by Mn^{III}(tpp)Cl, Mn^{III}(salen)Cl or Fe^{III}(tpp)Cl using iodosobenzene as the oxygen donor at room temperature leads to a slight decrease of the imine yield compared with the uncatalysed reaction. For instance 46% of **2a** is formed with iodosobenzene as the oxidant at this temperature after 0.5 h reaction time, whereas in the presence of Fe(tpp)Cl as the catalyst only 34% is formed under the same reaction conditions after 0.5 h. Furthermore benzaldehyde is also formed in 18% yield. It has been observed for these transition-metal-catalysed reactions, that some cleavage products and other oxidized by-products are formed.

It has been found that the substrates **1a–c**, **e**, **g**, **h** which are oxidized to the corresponding imines, **2a–c**, **e**, **g**, **h**, in high yields at room temperature with iodosobenzene as oxidant, cannot be oxidized to the imine in higher yield when a metal catalyst is present at the same temperature. This is probably due to the reactive oxo-transition metal complex intermediate formed in these reactions which can cleave the imine.[7] If the reaction temperature is reduced to 0 °C an increased reaction rate for the metal-catalysed oxidation of the amines is observed compared to the uncatalysed reaction.

The results for the oxidation of **1a** at 0 °C with and without either Mn^{III}(tpp)Cl, Mn^{III}(salen)Cl or Fe^{III}(tpp)Cl present and iodosobenzene as the oxygen donor are given as the first four entries of Table 2.

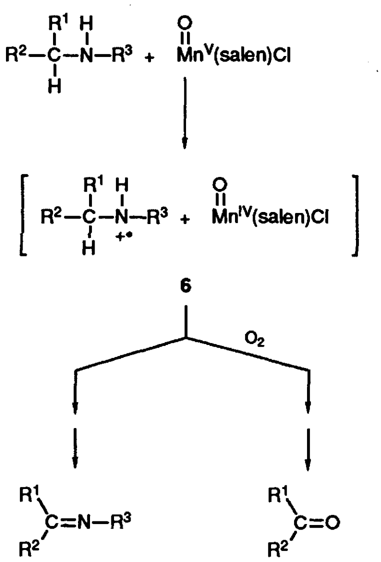
Imine **2a** is formed in 31% yield with iodosobenzene as the oxidant after 2 h at 0 °C (entry 1). A higher yield of **2a** is obtained when either Mn^{III}(tpp)Cl, Mn^{III}(salen)Cl or Fe^{III}(tpp)Cl is present as the catalyst (entries 2, 3, 4). Dibenzylamine, **1e** (entry 9) gives, besides the expected corresponding imine, **2e** [in low yield compared with the uncatalysed reaction (entry 8)], small amounts of the corresponding nitrone and benzaldehyde. Compound **1f** gives only 16% of the imine, **2f**, after 46 h with iodosobenzene as the oxidant at room temperature (entry 10), but 65% of **2f** is obtained after only 2 h with Fe^{III}(tpp)Cl as the catalyst at the same reaction temperature (entry 11). Mn^{III}(salen)Cl and Mn^{III}(tpp)Cl also catalyse the oxidation of **1f** to **2f** (entries 12, 13). Pivalic acid is formed as a by-product in these reactions. Compound **1i** can be oxidized to the corresponding imine by the catalytic system in slightly better yield than the uncatalysed reaction (not shown in Table 2). Diisopropylamine, **1j**, which is nearly inert to oxidation to the corresponding imine, **2j**, with iodosobenzene as the oxidant (entry 14) can be oxidized to **2j** in reasonable yield in the presence of the iron and manganese catalysts. The best yield of **2j** is found when Mn^{III}(tpp)Cl is the catalyst (entry 16) with only a small amount of the nitrone compared with the reaction catalysed by Mn^{III}(salen)Cl.

Sodium hypochlorite can also be used as an oxygen donor for the transition-metal-catalysed oxidation, but compared with iodosobenzene it is less effective.

The oxidation of Ph–CH$_2$–NH–C(CH$_3$)$_3$ and Ph–CD$_2$–NH–C(CH$_3$)$_3$ catalysed by Mn^{III}(salen)Cl with iodosobenzene as the oxygen donor has also been studied, but no significant isotope effect was found (<1.2). This result indicates, as in the uncatalysed reaction, that breaking of the C–H bond is probably not the rate-determining step.

The oxidations of **3a**, **c–e** and **4a**, **c–e** in the presence of Mn^{III}(salen)Cl as catalyst and iodosobenzene as the terminal oxidation reagent have also been performed in order to construct a Hammett plot for the disappearance of the amines. The observed variation in reaction rate for the oxidations of **3a**, **c–e** correlates poorly with σ (correlation coefficient: 0.83), and with other Hammett σ values. The following rate constants are obtained at 0 °C for the oxidation of **4a**, **c–e**, 8.1×10^{-7} s^{-1}, 42.6×10^{-7} s^{-1}, 6.1×10^{-7} s^{-1} and 2.5×10^{-7} s^{-1}, respectively. These values correlate with σ^+ and give ρ as -0.8 (correlation coefficient: 0.98).

The first step in the reaction between the oxygen donor and the metal complex is proposed to be the formation of an oxo-metal species which is the reactive intermediate in these reactions.[4,8] The Hammett plots for oxidation of the amines by either iodosobenzene or by a Mn^{III}(salen)Cl–iodosobenzene system indicate that different reaction mechanisms are probably operating, as they correlate with σ, or σ^+ respectively. A possible mechanism for the oxidation of amines to imines with iodosobenzene has been outlined in Scheme 1. The fact that the reaction rate for the disappearance of **4a**, **c–e** in the Mn^{III}(salen)Cl-catalysed reaction correlates with σ^+ might indicate that the first step here could be a one-electron transfer from the amine to O=Mn^{V}(salen)Cl giving O=Mn^{IV}(salen)Cl and an amine cation radical intermediate as outlined in Scheme 2. A one-electron transfer from the amine to an acceptor system would be expected to give a small deuterium effect,[5,9] in accordance with our findings. The initial step in the metalloporphyrin-catalysed iodosobenzene oxidation of *N*,*N*-dimethylbenzylamine has been suggested to take place *via* an



Scheme 2

initial electron transfer from the amine to a high valent oxo-metal species.[5] Furthermore, one-electron transfer reactions have been observed previously in the oxidation of amines as *e.g.* in the reaction of substituted benzyldimethylamines with chlorine dioxide.[9a,10] A one-electron transfer to a high valent O=Mn^{V}(salen)Cl intermediate is not without precedent in the oxidation of other substrates, as *e.g.* the reaction of alkenes with oxo-manganese(V) or oxo-iron(V) porphyrins which has been proposed to take place *via* a one-electron transfer from the alkene to the oxo-metal(V) species.[11]

From the amine cation radical–O=Mn^{IV}(salen)Cl complex, **6**, there could be two possible reaction paths; the oxidation to the imine or a reaction with molecular oxygen to give a carbonyl compound, as the latter is observed as the major by-product in these reactions. It is found that oxidation of **1a** under anaerobic conditions catalysed by Mn^{III}(salen)Cl and iodosobenzene as the terminal oxidant leads to a reaction with less than 2% of benzaldehyde formation, indicating that molecular oxygen might be involved in the formation of the carbonyl compound. An aminium cation might also be formed from **6** which could lead to the carbonyl compound.[10] The formation of the nitrone in some of these reactions could take place along the reaction path from the amine cation radical, as we have found that only small amounts of nitrones are formed when imines are oxidized by the Mn^{III}(tpp)Cl–iodosobenzene system.[7]

Conclusion

It has been shown that secondary amines can be oxidized to the corresponding imines by iodosobenzene or by a Mn^{III}(tpp)Cl, Mn^{III}(salen)Cl or Fe^{III}(tpp)Cl catalysed reaction with iodosobenzene as the terminal oxidant. With iodosobenzene as the oxidant both aromatic and aliphatic amines are oxidized in good yields to the corresponding imines and the elimination takes place towards the least substituted carbon. The reaction shows no significant isotope effect and Hammett plots for the disappearance of the amines correlates with σ. The experimental results support a mechanism by which the lone pair electrons of the nitrogen in the secondary amine attack the iodine of iodosobenzene, followed by a decomposition to water, iodobenzene and the imine. The metal-catalysed oxidation probably takes place in a different way. These catalysed reactions can be used for amine substrates which are difficult to oxidize with iodosobenzene, but they are complicated by the formation of by-products. A Hammett plot for the oxidation of a series of amines shows correlation with σ^+, rather than with σ. Again no significant isotope effect could be found in these reactions. It is suggested that this reaction proceeds by a one-electron transfer from the amine to the putative oxo-metal(V) intermediate species with formation of an amine cation radical and an oxo-metal(IV) species. The reaction is terminated by a further oxidation of the amine cation radical to the imine.

Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 200 spectrometer. $SiMe_4$ was used as internal standard. Mass spectra were recorded on a Micro-Mass 7070F or Trio-2 spectrometer operating at 70 eV with a direct inlet.

Materials.—Iodosobenzene was synthesized according to the literature[12] and stored under vacuum. It is important for successful results that iodosobenzene is dried for more than 3 weeks and crushed carefully before use. Sodium hypochlorite (15%) was used as received from Bie and Berntsen. Some of the amines were commercially available, others were prepared by reduction of the imines by $NaBH_4$.[13] The imines were synthesized according to the literature.[14] The amines were distilled and dried before use. Chloro(5,10,15,20-tetraphenylporphyrinato)-iron(III) and -manganese(III) [Fe^{III}(tpp)Cl and Mn^{III}(tpp)Cl] are available from Aldrich, while Mn^{III}(salen)Cl was prepared according to the literature.[15] The solvents were refluxed over potassium permanganate–potassium carbonate for 24 h and distilled before use.

General Procedure for the Oxidation of Amines to Imines with Iodosobenzene as the Oxidation Reagent.—The amine (0.5 mmol) was dissolved in CH_2Cl_2 (5 cm^3), iodosobenzene (1.0 mmol) was added at room temperature, the solution was stirred for the time given in Table 1. After completion the reaction mixture was filtered through Celite and solvent removed to give the oxidized products. The products were identified by ^{1}H NMR spectroscopy and MS or GC–MS techniques.

General Procedure for the Oxidation of Amines to Imines Catalysed by Mn^{III}(tpp)Cl, Fe^{III}(tpp)Cl *or* Mn^{III}(salen)Cl *as the Catalyst and with Iodosobenzene as the Oxidation Reagent.*—The amine (0.5 mmol) and the catalyst (0.025 mmol) were dissolved in CH_2Cl_2 (5 cm^3), iodosobenzene (1.0 mmol) was added at 0 °C, and the solution was stirred for the time given in Table 2. After completion of the reaction the mixture was filtered through Celite and the solvent removed. Then the mixture was washed with pentane, filtered through Celite to remove the catalyst and evaporated to give the products. The products were identified by ^{1}H NMR spectroscopy and MS or GC–MS techniques.

The reaction in the presence of the nitrone was performed as in the general procedure, but with the presence of 2 mmol of the radical trap. The products were analysed by ^{1}H NMR spectroscopy.

Kinetic Experiments.—The experiments with **3a–e** and **4a–e** and iodosobenzene only were performed with 0.15 mmol of the amine and 0.30 mmol of iodosobenzene dissolved in 1 cm^3 $CDCl_3$ in a NMR tube and monitored by ^{1}H NMR spectroscopy at 20 °C. In the metal-catalysed reactions the amine (0.5 mmol) and the catalyst (0.025 mmol) were dissolved in CH_2Cl_2 (5 cm^3) and iodosobenzene (1.0 mmol) was added. The reaction mixture was kept at 0 °C and at different times a small fraction was taken out, filtered through Celite (to remove iodosobenzene) and the solvent removed. Then it was washed with pentane, filtered through Celite to remove the catalyst and the solvent evaporated. The reaction mixture was analysed by ^{1}H NMR spectroscopy.

The ^{1}H NMR data for the imines are as follows (δ values given relative to SiMe$_4$). **2a**: 1.30 [s, 9 H, C(CH$_3$)$_3$], 7.38–7.42 (m, 3 H, Ph), 7.73–7.78 (m, 2 H, Ph), 8.28 (s, 1 H, CH). **2b**: 1.26 (d, 6 H, 2 × CH$_3$), 3.54 (sep, 1 H, N–CH$_2$), 7.37–7.41 (m, 3 H, Ph), 7.70–7.75 (m, 2 H, Ph), 8.30 (s, 1 H, CH=N). **2c**: 1.31 (t, 3 H, CH$_3$), 3.65 (q, 2 H, CH$_2$), 7.39–7.42 (m, 3 H, Ph), 7.70–7.75 (m, 2 H, Ph), 8.30 (s, 1 H, CH). **2d**: 7.19–7.26 (m, 3 H, Ph), 7.35–7.49 (m, 5 H, Ph), 7.88–7.93 (m, 2 H, Ph), 8.45 (s, 1 H, CH). **2e**: 4.82 (s, 2 H, CH$_2$), 7.23–7.43 (m, 8 H, Ph); 7.76–7.81 (m, 2 H, Ph), 8.37 (s, 1 H, CH). **2f**: 1.18 [s, 9 H, C(CH$_3$)$_3$], 6.98–7.02 (d, 2 H, Ph), 7.10–7.19 (t, 2 H, Ph), 7.28–7.36 (t, 2 H, Ph), 7.68 (s, 1 H, CH). **2g**: 2.75 (t, 2 H, CH$_2$), 3.77 (t, 2 H, N–CH$_2$), 7.27–7.37 (m, 4 H, Ar), 8.34 (s, 1 H, CH). **2h**: 0.91 (t, 3 H, CH$_3$), 0.95 (t, 3 H, CH$_3$), 1.25–1.64 (m, 6 H, 3 × CH$_2$), 2.20 (q, 2 H, CH$_2$), 3.35 (t, 2 H, N–CH$_2$), 7.62 (t, 1 H, CH). **2i**: 1.07 (t, 3 H, CH$_3$, 1.19–1.84 (m, 10 H, 5 × CH$_2$), 2.22 (dq, 2 H, CH$_2$), 2.89 (m, 1 H, N–CH), 7.66 (s, 1 H, CH). **2j**: 1.10 [d, 6 H, (CH$_3$)$_2$], 1.84 (s, 3 H, CH$_2$), 1.98 (s, 3 H, CH$_3$), 3.60 (sep, 1 H, CH).

The ^{1}H NMR data for the nitrones are as follows (δ values given relative to SiMe$_4$). PhCH=N(O)CH$_2$Ph: 5.06 (s, 2 H, CH$_2$), 7.36–7.51 (m, 9 H, Ph, CH), 8.17–8.25 (m, 2 H, Ph). (CH$_3$)$_2$C=N(O)CH(CH$_3$)$_2$: 1.37 (d, 6 H, CH$_3$), 2.14 (s, 6 H), CH$_3$), 4.47 (sep, 1 H, CH).

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