Iron-catalysed Oxidation of *N,N*-(Dialkyl)acylmethylamines with Molecular Oxygen in the Presence of either 2-Mercaptoethanol or Sodium Sulphide

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Air-oxidation of *N,N*-(dialkyl)acylmethylamines (**1a–f**) using a catalytic amount of [{Fe(salen)}$_2$O] [salen = *N,N'*-bis(salicylidene)ethylenediaminato] in the presence of 2-mercaptoethanol gave the corresponding α-oxo amides (**2a–f**) in moderate to good yields. With sodium sulphide in place of the thiol α-oxo thioamides (**9a–f**) were obtained as the predominant products.

Oxidative functionalisation of amines at the α-position to nitrogen is a useful tool for synthesis of alkaloids and amino acids.[1] Another important feature of amine oxidation, especially catalysed by iron complexes, is of relevance to enzymatic *N*-dealkylation in biological systems and various model reactions for cytochrome P-450 and other iron-containing proteins have also been reported.[2]

As part of our study of the oxidation of nitrogen-containing compounds with molecular oxygen using iron complexes,[3] we have undertaken the air-oxidation of *N,N*-(dialkyl)acylmethylamines (**1a–f**) with [{Fe(salen)}$_2$O] [salen = *N,N'*-bis(salicylidene)ethylenediaminato] in the presence of either 2-mercaptoethanol or sodium sulphide, expecting that they would be transformed into the corresponding α-oxo amides (**2a–f**) which are useful materials for synthesis of heterocyclic compounds.[4]

Results and Discussion

Oxidation of N-(*Benzoylmethyl*)*piperidine* (**1a**) *in the Absence of Sulphur-containing Compounds.*—When a solution of the amine (**1a**) (2 mmol) in acetonitrile containing [{Fe(salen)}$_2$O] (0.15 mmol) was stirred at 20 °C under oxygen (1 atm) for 2 h, 1.8 mmol of oxygen was consumed after a short induction period; formation of *N*-(benzoylcarbonyl)piperidine (**2a**) (7%) together with benzoic acid (**3a**) (33%) and *N*-formylpiperidine (**4a**) (16%) was detected (Table 1 and Figure 1). The reaction did not proceed in the absence of the iron complex. While addition of 2,6-di-t-butyl-4-methylphenol (BHT) did not completely inhibit the reaction, the rate of oxygen uptake was somewhat retarded. The reaction in pyridine was extremely slow. These trends are similar to those found in enamine oxidation with oxygen using iron or copper salts[5] and suggest that the oxygenation of (**1a**) proceeds *via* its co-ordination to the iron complex. The key intermediate leading to the products would be the hydroperoxide (**5**) (Scheme 1).[6]

Oxidation of the Amines (**1a–f**) *in the Presence of* 2-*Mercaptoethanol.*—When the oxidation of (**1a**) (2 mmol) was carried out in the presence of 2-mercaptoethanol (4 equiv.), 3.5 mmol of oxygen was consumed to give the α-oxo amide (**2a**) in a yield of 59% along with bis-(2-hydroxyethyl) disulphide (91%) (Table 1).† A more satisfactory yield of (**2a**) (70%) was obtained under air. Addition of benzenethiol in place of 2-mercaptoethanol also increased the yield of (**2a**) considerably, but with diphenyl sulphide no meaningful effect was observed. While other iron species [Fe(salen)]OAc, [Fe(tpp)]OAc(tpp = *meso*-tetraphenylporphyrinato), [$Fe_3O(OAc)_6(py)_3$] (py = pyridine), and $FeCl_3$ could also be used, they appeared to be less effective than [{Fe(salen)}$_2$O]. The α-oxo amides (**2b–f**) were also obtained in moderate to good yields from the reactions of (**1b–f**) using [{Fe(salen)}$_2$O].‡

$R^1C(:O)CH_2NR^2R^3$

(**1**)
a; R^1 = Ph, R^2,R^3 = $-(CH_2)_5-$
b; R^1 = 4-MeC_6H_4, R^2,R^3 = $-(CH_2)_5-$
c; R^1 = 4-ClC_6H_4, R^2,R^3 = $-(CH_2)_5-$
d; R^1 = Ph, R^2,R^3 = $-(CH_2)_4CHMe-$
e; R^1 = Ph, R^2 = R^3 = Et
f; R^1 = Me, R^2,R^3 = $-(CH_2)_5-$

$R^1C(:O)C(:O)NR^2R^3$

(**2**)
a; R^1 = Ph, R^2,R^3 = $-(CH_2)_5-$
b; R^1 = 4-MeC_6H_4, R^2,R^3 = $-(CH_2)_5-$
c; R^1 = 4-ClC_6H_4, R^2,R^3 = $-(CH_2)_5-$
d; R^1 = Ph, R^2,R^3 = $-(CH_2)_4CHMe-$
e; R^1 = Ph, R^2 = R^3 = Et
f; R^1 = Me, R^2,R^3 = $-(CH_2)_5-$
g; R^1 = Ph, R^2,R^3 = $-(CH_2)_4-$
h; R^1 = 2-naphthyl, R^2,R^3 = $-(CH_2)_5-$

R^1CO_2H

(**3**)
a; R^1 = Ph
b; R^1 = 4-MeC_6H_4
c; R^1 = 4-ClC_6H_4
d; R^1 = 2-naphthyl

$HC(:O)NR^1R^2$

(**4**)
a; R^2, R^3 = $-(CH_2)_5-$
b; R^2, R^3 = $-(CH_2)_4CHMe-$

A possible role of the added thiol could be its co-ordination to the complex and reduction to a Fe^{II} species which then reacts with molecular oxygen to generate the active oxidant.[7] Another possibility would be that it reduces the hydroperoxide (**5**) to the α-amino alcohol (**6**) (Scheme 1). It was confirmed that (*a*) a small amount of phenylglyoxal (**7a**) (a few %) was formed in the early stage of the reaction of (**1a**) (by GLC–MS analysis) and (*b*) the reaction of phenylglyoxal (**7a**) in the presence of piperidine (**8a**) under the same conditions used for (**1a**) gave the oxo amide (**2a**) along with (**3a**) even in the absence of the thiol (Scheme 2 and Table 2; see also next section). These results might suggest that the reduction of (**5**) to (**6**) is the major function of the thiol added. However, in the reaction of (**7a**) with (**8a**), excess of (**8a**) or a higher temperature was needed to obtain a reasonable yield of (**2a**). Therefore, further elucidation is required to clarify the mode of action of the thiol.

† The iron complex was found to be an effective catalyst for oxidation of thiols to the corresponding disulphides.[8]
‡ The relevant oxidation of α-amino ketones using mercury(II) acetate,[9a] lead tetra-acetate,[9b,c] mercury(II)–ethylenediaminetetra-acetic acid (EDTA),[9c] hydrogen peroxide,[9c,d] sodium metaperiodate,[9c] and manganese dioxide[9c] has been reported, where cleaved products (acids, glyoxals, or α-diketones) are predominantly produced.

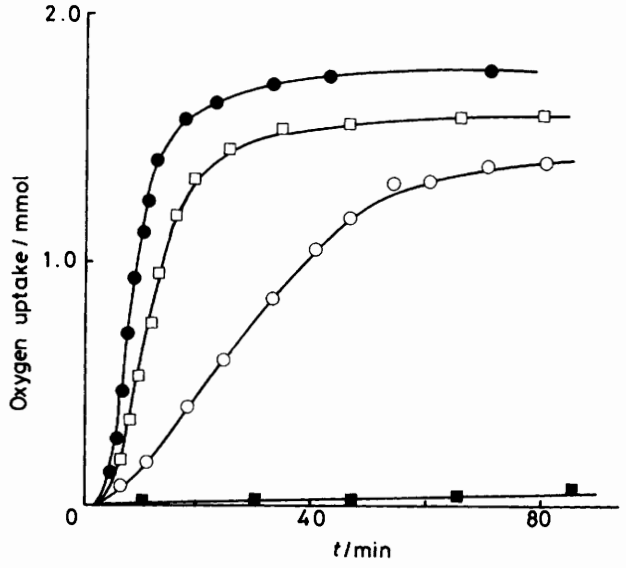
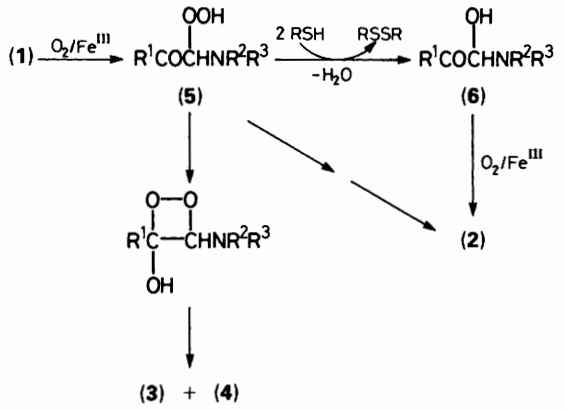


Figure 1. Oxygen uptake in the oxidation of the amine (**1a**) (2 mmol) in the presence of [{Fe(salen)}$_2$O] (0.15 mmol) at 20 °C. (●) In acetonitrile, (■) in pyridine, (○) in pyridine–water (5:1, v/v), (□) in acetonitrile in the presence of BHT (2 mmol).



Scheme 1.

Oxidative Coupling of Arylglyoxals (**7a–c**) *with Secondary Amines* (**8a–d**).—The reaction of (**7a**) (2 mmol) with (**8a**) (8 equiv.) in the presence of [{Fe(salen)}$_2$O] (0.15 mmol) in acetonitrile at 20 °C under oxygen consumed 1.9 mmol of oxygen during 5 h to give the oxo amide (**2a**) (74%) along with the acid (**3a**) (20%) (Table 2 and Figure 2). This reaction was also considerably retarded by addition of BHT. In contrast with (**1a**), the reaction in pyridine was as fast as that in acetonitrile, suggesting that the first step of the oxidation is different from that of (**1a**). However, the details are unclear.

The reaction of arylglyoxals (**7a–c**) with secondary amines (**8a–d**) in the presence of [{Fe(salen)}$_2$O] at 60 °C gave the corresponding α-oxo amides in moderate to good yields. This method as a route to aroylformamides seems to be useful, since arylglyoxals can be conveniently prepared by oxidation of the corresponding aryl methyl ketones with hydrobromic acid–dimethyl sulphoxide.[10]

Oxidation of the Amines (**1a–f**) *in the Presence of Sodium Sulphide*.—When the oxidation of (**1a**) (2 mmol) in the presence of [{Fe(salen)}$_2$O] (0.15 mmol) was carried out using sodium sulphide (2 mmol) in place of 2-mercaptoethanol in pyridine–water (5:1, v/v) at 20 °C for 2 h under air, 1.7 mmol of the oxygen in the air was consumed during this period. It was of interest that the predominant product was *N*-(benzoylthiocarbonyl)piperidine (**9a**) (75%) (Scheme 3 and Table 3).* It was also confirmed that the reaction did not proceed in the absence of the iron complex or under nitrogen. The yield of (**9a**), however, decreased considerably either in acetonitrile–water or under pure oxygen. While [Fe(salen)]OAc could also be used, with [Fe(tpp)]OAc the acid (**3a**) was the major product. The other iron species [$Fe_3O(OAc)_6(py)_3$] and $FeCl_3$ were ineffective. The α-oxo thioamides (**9b–f**) were also obtained in moderate to good yields from the reactions of (**1b–f**) using [{Fe(salen)}$_2$O].

The present thioxisation appears to be similar to the

* The conditions are somewhat similar to those in the Gif system.[11]

Table 1. Oxidation of *N*,*N*-(dialkyl)acylmethylamines (**1a–f**) in the presence of 2-mercaptoethanol.[a]

Amine	Products (yield, %)[b]	% Recovery of (**1**)[b]
(**1a**)[c,d]	(**2a**) (7), (**3a**) (33), (**4a**) (16)	5
(**1a**)[d]	(**2a**) (59), (**3a**) (12), (**4a**) (6)	2
(**1a**)	(**2a**) (70), (**3a**) (10)	2
(**1a**)[e]	(**2a**) (38), (**3a**) (9), (**4a**) (11)	9
(**1a**)[f]	(**2a**) (11), (**3a**) (36), (**4a**) (20)	30
(**1a**)[g]	(**2a**) (65), (**3a**) (4)	6
(**1a**)[h]	(**2a**) (56), (**3a**) (14), (**4a**) (9)	2
(**1a**)[i]	(**2a**) (39), (**3a**) (29), (**4a**) (17)	1
(**1a**)[j]	(**2a**) (13), (**3a**) (14), (**4a**) (8)	12
(**1a**)[k]	(**2a**) (42)[l]	
(**1b**)	(**2b**) (58), (**3b**) (6), (**4a**) (6)	6
(**1c**)	(**2c**) (76), (**3c**) (1)	18
(**1d**)	(**2d**) (32), (**3a**) (11), (**4b**) (2)	17
(**1e**)	(**2e**) (32), (**3a**) (7)	14
(**1f**)	(**2f**) (20), (**3a**) (1)	63

[a] The reaction of (**1**) (2 mmol) was carried out in the presence of [{Fe(salen)}$_2$O] (0.15 mmol) and 2-mercaptoethanol (8 mmol) in acetonitrile under air at 20 °C for 2 h unless otherwise noted. [b] Determined by GLC analysis. [c] In the absence of the thiol. [d] Under oxygen. [e] Reaction with benzenethiol (8 mmol). [f] Reaction with diphenyl sulphide (8 mmol). [g] [Fe(salen)]OAc (0.3 mmol). [h] [Fe(tpp)]OAc (0.3 mmol). [i] [$Fe_3O(OAc)_6(py)_3$] (0.1 mmol). [j] $FeCl_3$ (0.3 mmol). [k] Reaction using (**1a**) (25 mmol), [{Fe(salen)}$_2$O] (1.9 mmol), and 2-mercaptoethanol (100 mmol) with bubbling air for 5 h. [l] After isolation. The yield of the other products was not determined.

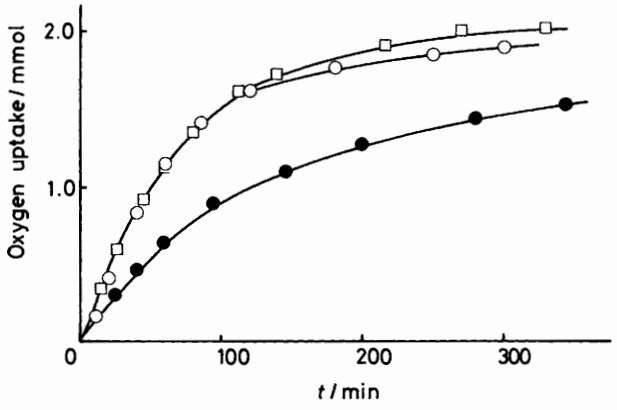


Figure 2. Oxygen uptake in the reaction of (**7a**) (2 mmol) with (**8a**) (16 mmol) in the presence of [{Fe(salen)}$_2$O] (0.15 mmol) at 20 °C. (○) In acetonitrile, (□) in pyridine, (●) in acetonitrile in the presence of BHT (2 mmol).

$$R^1C(:O)C(:O)H + HNR^2R^3 \xrightarrow[MeCN]{O_2\text{-}[\{Fe(salen)\}_2O]} (2) + (3)$$

(7)
a; R^1 = Ph
b; R^1 = 4-ClC_6H_4
c; R^1 = 2-naphthyl

(8)
a; R^2,R^3 = $-(CH_2)_5-$
b; R^2,R^3 = $-(CH_2)_4CHMe-$
c; R^2 = R^3 = Et
d; R^2,R^3 = $-(CH_2)_4-$

Scheme 2.

Table 2. Oxidative coupling of arylglyoxals (**7a–c**) and secondary amines (**8a–d**).[a]

Glyoxal	Amine (mmol)	Temp. °C	Cat. (mmol)	Products (yield, %)[b]
(**7a**)	(**8a**) (2)[c]	20	0.15	(**2a**) (11), (**3a**) (33)
(**7a**)	(**8a**) (16)[c]	20	0.15	(**2a**) (45), (**3a**) (2)
(**7a**)	(**8a**) (2)	20	0.15	(**2a**) (5), (**3a**) (3)
(**7a**)	(**8a**) (16)	20	0.15	(**2a**) (62), (**3a**) (14)
(**7a**)	(**8a**) (16)[d,e]	20	0.15	(**2a**) (74), (**3a**) (20)
(**7a**)	(**8a**) (16)	20	—[f]	(**2a**) (9), (**3a**) (1)
(**7a**)	(**8a**) (2)[d]	60	0.05	(**2a**) (68), (**3a**) (19)
(**7a**)	(**8a**) (16)[d]	60	0.05	(**2a**) (82), (**3a**) (17)
(**7a**)	(**8b**) (16)[d]	60	0.05	(**2d**) (32), (**3a**) (30)
(**7a**)	(**8c**) (16)[d]	60	0.05	(**2e**) (28), (**3a**) (19)
(**7a**)	(**8d**) (16)[d]	60	0.05	(**2g**) (77), (**3a**) (13)
(**7b**)	(**8a**) (16)[d]	60	0.05	(**2c**) (70), (**3c**) (5)
(**7c**)	(**8a**) (16)[d]	60	0.05	(**2h**) (81), (**3d**) (15)
(**7c**)	(**8a**) (160)[d,g]	60	0.5	(**2h**) (75)[h]

[a] The reaction of (**7**) (2 mmol) with (**8**) was carried out in the presence of [{Fe(salen)}$_2$O] in acetonitrile at 20 °C under air for 2 h unless otherwise noted. [b] Yield determined by GLC analysis. [c] Reaction in the presence of 2-mercaptoethanol (8 mmol). [d] Reaction under oxygen. [e] Reaction for 5 h. [f] Reaction in the absence of the iron complex. [g] Reaction with (**7c**) (20 mmol). [h] After isolation. The yield of the other products was not determined.

Table 3. Oxidation of *N,N*-(dialkyl)acylmethylamines (**1a–f**) in the presence of sodium sulphide.[a]

Amine	Products (yield, %)[b]	% Recovery of (**1**)[b]
(**1a**)	(**9a**) (75), (**2a**) (4), (**3a**) (3)	11
(**1a**)[c]	(**9a**) (17), (**2a**) (2), (**3a**) (10)	13
(**1a**)[d]	(**9a**) (35), (**2a**) (9), (**3a**) (15)	12
(**1a**)[e]	(**9a**) (60), (**2a**) (4), (**3a**) (6)	18
(**1a**)[f]	(**9a**) (13), (**2a**) (7), (**3a**) (40)	5
(**1a**)[g]	(**2a**) (4), (**3a**) (6)	85
(**1a**)[h]	(**2a**) (4)	86
(**1a**)[i]	(**9a**) (34), (**2a**) (4), (**3a**) (3)	7
(**1a**)[i,j]	(**9a**) (11), (**3a**) (1)	71
(**1a**)[i,k]	(**9a**) (18)	51
(**1a**)[l]	(**9a**) (50)[m]	
(**1b**)	(**9b**) (43), (**2b**) (5), (**3b**) (25)	5
(**1c**)	(**9c**) (78), (**2c**) (3), (**3c**) (6)	10
(**1d**)	(**9d**) (52), (**2d**) (5), (**3a**) (7)	26
(**1e**)	(**9e**) (47), (**2e**) (3), (**3a**) (12)	18
(**1f**)[n]	(**9f**) (13), (**2f**) (6)	14

[a] The reaction of (**1**) (2 mmol) was carried out in the presence of [{Fe(salen)}$_2$O] (0.15 mmol) and sodium sulphide (2 mmol) in pyridine–water (5:1, v/v) under air at 20 °C for 2 h unless otherwise noted. [b] Determined by GLC analysis. [c] Reaction in acetonitrile–water (5:1, v/v). [d] Reaction under oxygen. [e] [Fe(salen)]OAc (0.3 mmol). [f] [Fe(tpp)]OAc (0.3 mmol). [g] [$Fe_3O(OAc)_6(py)_3$] (0.1 mmol). [h] $FeCl_3$ (0.3 mmol). [i] Reaction with elemental sulphur (2 mmol). [j] In the absence of the iron complex. [k] Reaction under nitrogen. [l] Reaction using (**1a**) (25 mmol), [{Fe(salen)}$_2$O] (1.9 mmol), and sodium sulphide (25 mmol) with bubbling air for 5 h. [m] After isolation. The yield of the other products was not determined. [n] Reaction at 60 °C.

Willgerodt–Kindler reaction.[12] The related reaction (1) of the enamine (**10**) with elemental sulphur to give the thioamide (**11**) has been reported, in which 'activated sulphur' formed in the reaction medium is considered to be the active species.[13] Compounds (**1**) would exist partly in the enamine form by enolisation under the reaction conditions.

$$\underset{(10)}{R^1CH(NR^2_2)CH=CH_2} \xrightarrow{S_8} \underset{(11)}{R^1CH_2C(:S)NR^2_2} \quad (1)$$

The fact that the rate of the oxidation of (**1a**) in pyridine–water is slow (Figure 1) and the yield of (**9a**) decreased under oxygen led us to deduce that the present reaction also involves an active sulphur species generated from the reaction of sodium sulphide with oxygen mediated by the iron complex prior to the oxygenation of (**1**). In connection with this, we carried out the reaction of (**1a**) using sulphur in place of sodium sulphide (Table 3); the thioamide (**9a**) was also produced even under nitrogen or in the absence of the iron complex, although the yield was low.

While several methods for preparation of α-oxo thioamides have been reported,[14] the present thioxisation seems to be advantageous in some respects; the reaction can be carried out under mild conditions using reagents which are easily handled.

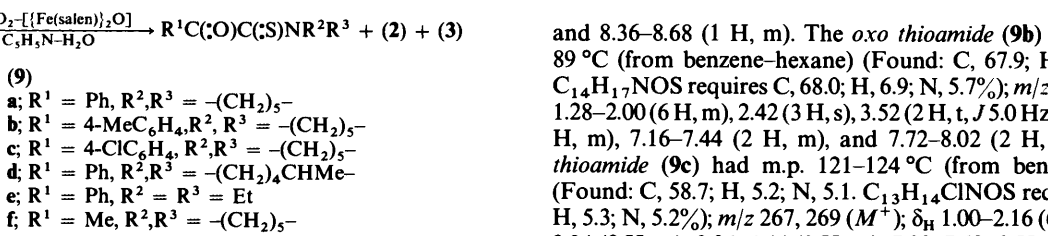
Experimental

^{1}H NMR spectra were obtained with a JEOL JNM-PS-100 spectrometer for $CDCl_3$ solutions. GLC–MS data were obtained with a JEOL JMS-DX-303 spectrometer. GLC analysis was carried out with a Shimadzu GC-8A gas chromatograph.

N,N-(Dialkyl)aroylmethylamines (**1a–e**) were prepared by the reaction of the corresponding aryl bromomethyl ketones[15] with secondary amines in ether.[16] The amine (**1f**),[17] arylglyoxals (**8a–c**),[10] and the iron complexes [{Fe(salen)}$_2$O],[18] [Fe(salen)]OAc,[18] [Fe(tpp)]OAc,[19] and [$Fe_3O(OAc)_6(py)_3$][20] were prepared by the methods reported previously. Other starting materials were commercially available. The following experimental details may be regarded as typical in methodology and scale. Larger scale reactions of (**1a**) (5.08 g, 25 mmol) with 2-mercaptoethanol, (**7c**) (3.68 g, 20 mmol) with (**8a**), and (**1a**) (5.08 g, 25 mmol) with sodium sulphide were also examined (Tables 1–3).

Oxidation of N-(*Benzoylmethyl*)*piperidine*(**1a**) *with Oxygen.*—The iron complex [{Fe(salen)}$_2$O] (99 mg, 0.15 mmol) was added to a flask equipped with a gas burette and a rubber cap. After the atmosphere in the flask and the gas burette had been replaced with oxygen, a solution of the amine (**1a**) (407 mg, 2 mmol) in acetonitrile (6 ml) was added *via* a syringe and resulting mixture was stirred at 20 °C for 2 h. Formation of the oxo amide (**2a**) (30 mg, 7%) and the formamide (**4a**) (36 mg, 16%) was confirmed by GLC–MS and GLC analyses. The mixture was poured into aqueous potassium carbonate and extracted with ether; the oxo amide (**2a**) (22 mg, 5%) was isolated by column chromatography on silica gel using hexane–ethyl acetate as eluant. The oxo amide (**2a**) had m.p. 108–110 °C (from benzene–hexane) (lit.,[21] 106 °C); *m/z* 217 (M^+); δ_H 1.40–2.05 (6 H, m), 3.20–3.42 (2 H, m), 3.60–3.80 (2 H, m), and 7.20–8.20 (5 H, m). Acidification of the aqueous phase with dilute hydrochloric acid and re-extraction with ether gave benzoic acid (**3a**) (81 mg, 33%). The yield was also determined by GLC analysis after trimethylsilylation with *N,O*-bis(trimethylsilyl)acetamide.

Air-oxidation of N-(*Benzoylmethyl*)*piperidine* (**1a**) *in the Presence of* 2-*Mercaptoethanol.*—A mixture of (**1a**) (407 mg, 2



Scheme 3.

mmol), [{Fe(salen)}$_2$O] (99 mg, 0.15 mmol), and 2-mercaptoethanol (156 mg, 2 mmol) in acetonitrile (6 ml) was stirred under air at 20 °C for 2 h. During the reaction, three portions of the thiol (156 mg, 2 mmol) in acetonitrile (0.5 ml) were also added at intervals of 30 min. Analysis by GLC–MS and GLC confirmed formation of (**2a**) (304 mg, 70%), (**3a**) (24 mg, 10%), and bis-(2-hydroxyethyl) disulphide (586 mg, 95%). The oxo amide (**2a**) (252 mg, 58%) was isolated by column chromatography on silica gel.

Oxidative Coupling of Phenylglyoxal (**7a**) *and Piperidine* (**8a**).—A mixture of (**7a**) (268 mg, 2 mmol), (**8a**) (1 362 mg, 16 mmol), and [{Fe(salen)}$_2$O] (33 mg, 0.05 mmol) in acetonitrile (10 ml) was stirred under oxygen at 60 °C for 2 h. Formation of (**2a**) (356 mg, 82%) and (**3a**) (42 mg, 17%) was confirmed by GLC–MS and GLC analyses. The oxo amide (**2a**) (326 mg, 75%) was isolated by column chromatography on silica gel.

Oxidation of the Amine (**1a**) *under Air in the Presence of Sodium Sulphide*.—A mixture of (**1a**) (407 mg, 2 mmol), [{Fe(salen)}$_2$O] (99 mg, 0.15 mmol), and sodium sulphide nonahydrate (480 mg, 2 mmol) in pyridine (5 ml)–water (0.68 ml) was stirred under air at 20 °C for 2 h. Formation of (**2a**) (13 mg, 3%), (**3a**) (10 mg, 4%), and (**9a**) (350 mg, 75%) was confirmed by GLC–MS and GLC analyses. The oxo thioamide (**9a**) (327 mg, 70%) was isolated by column chromatography on silica gel using hexane–ethyl acetate as eluant; m.p. 83–84 °C (from benzene–hexane) (lit.,[14b] 79–81 °C) (Found: C, 67.0; H, 6.4; N, 6.0; S, 13.8. Calc. for $C_{13}H_{15}NOS$: C, 66.9; H, 6.5; N, 6.0; S, 13.7%); *m/z* 233 (M^+); δ_H 1.42–2.05 (6 H, m), 3.52 (2 H, t, *J* 5.0 Hz), 4.08–4.45 (2 H, m), and 7.16–8.02 (5 H, m).

Products.—The *oxo amide* (**2b**) was an oil (Found: C, 72.3; H, 7.5; N, 5.7. $C_{14}H_{17}NO_2$ requires C, 72.7; H, 7.4; N, 6.1%); *m/z* 231 (M^+); δ_H 1.20–1.86 (6 H, m), 2.42 (3 H, s), 3.29 (2 H, t, *J* 4.0 Hz), 3.56–3.84 (2 H, m), 7.04–7.48 (2 H, m), and 7.68–8.04 (2 H, m). The *oxo amide* (**2c**) had m.p. 54–55 °C (from benzene–hexane) (Found: C, 61.7; H, 5.5; N, 5.6; Cl, 14.3. $C_{13}H_{14}ClNO_2$ requires C, 62.0; H, 5.6; N, 5.6; Cl, 14.1%); *m/z* 251 and 253 (M^+); δ_H 1.25–2.00 (6 H, m), 3.28 (2 H, t, *J* 5.0 Hz), 3.56–3.85 (2 H, m), 7.16–7.56 (2 H, m), and 7.62–8.04 (2 H, m). The *oxo amide* (**2d**) was an oil (Found: C, 72.3; H, 7.4; N, 5.9. $C_{14}H_{17}NO_2$ requires C, 72.7; H, 7.4; N, 6.1%); *m/z* 231 (M^+); δ_H 1.20–2.05 (9 H, m), 2.65–4.00 (2 H, m), 4.40–5.05 (1 H, m), and 7.28–8.10 (5 H, m). The *oxo amide* (**2e**) was an oil;[22] *m/z* 231 (M^+); δ_H 1.13 (3 H, t, *J* 6.0 Hz), 1.28 (3 H, t, *J* 6.0 Hz), 3.25 (2 H, q, *J* 6.0 Hz), 3.57 (2 H, q, *J* 6.0 Hz), 7.24–7.77 (3 H, m), and 7.80–8.08 (2 H, m). The *oxo amide* (**2f**) was an oil;[23] *m/z* 155 (M^+); δ_H 1.40–1.89 (6 H, m), 2.21 (3 H, s), 3.37 (2 H, t, *J* 5.0 Hz), and 3.56 (2 H, t, *J* 5.0 Hz). The *oxo amide* (**2g**) was an oil;[22] *m/z* 225 (M^+) δ_H 1.68–2.20 (4 H, m), 3.43 (2 H, t, *J* 6.0 Hz), 3.67 (2 H, t, *J* 6.0 Hz), 7.28–7.80 (3 H, m), and 7.88–8.30 (2 H, m). The *oxo amide* (**2h**) had m.p. 80–81 °C (from benzene–hexane) (Found: C, 76.1; H, 6.4; N, 5.2. $C_{17}H_{17}NO_2$ requires C, 76.4; H, 6.4; N, 5.2%); *m/z* 267 (M^+); δ_H 1.20–2.04 (6 H, m), 3.31 (2 H, t, *J* 5.0 Hz), 3.60–4.08 (2 H, m), 7.20–7.68 (2 H, m), 7.72–8.28 (4 H, m), and 8.36–8.68 (1 H, m). The *oxo thioamide* (**9b**) had m.p. 88–89 °C (from benzene–hexane) (Found: C, 67.9; H, 6.9; N, 5.7. $C_{14}H_{17}NOS$ requires C, 68.0; H, 6.9; N, 5.7%); *m/z* 247 (M^+); δ_H 1.28–2.00 (6 H, m), 2.42 (3 H, s), 3.52 (2 H, t, *J* 5.0 Hz), 4.16–4.35 (2 H, m), 7.16–7.44 (2 H, m), and 7.72–8.02 (2 H, m). The *oxo thioamide* (**9c**) had m.p. 121–124 °C (from benzene–hexane) (Found: C, 58.7; H, 5.2; N, 5.1. $C_{13}H_{14}ClNOS$ requires C, 58.3; H, 5.3; N, 5.2%); *m/z* 267, 269 (M^+); δ_H 1.00–2.16 (6 H, m), 3.21–3.84 (2 H, m), 3.96–4.44 (2 H, m), 7.20–7.68 (2 H, m), and 7.72–8.26 (2 H, m). The *oxo thioamide* (**9d**) had m.p. 91–93 °C (from benzene–hexane) (Found: C, 67.8; H, 6.8; N, 5.5. $C_{14}H_{17}NOS$ requires C, 68.0; H, 6.9; N, 5.7%); *m/z* 247 (M^+); δ_H 1.20–2.16 (9 H, m), 3.00–4.30 (2 H, m), 5.28–6.00 (1 H, m), and 7.28–8.10 (5 H, m). The *oxo thioamide* (**9e**) was an oil (Found: C, 65.0; H, 6.8; N, 6.2; S, 14.1. $C_{12}H_{15}NOS$ requires C, 65.1; H, 6.8; N, 6.3; S, 14.5%); *m/z* 221 (M^+); δ_H 1.19 (3 H, t, *J* 7.5 Hz), 1.28 (3 H, t, *J* 7.5 Hz), 3.48 (2 H, q, *J* 7.5 Hz), 4.05 (2 H, q, *J* 7.5 Hz), and 7.24–8.22 (5 H, m). The *oxo thioamide* (**9f**) was an oil;[24] *m/z* 171 (M^+); δ_H 1.40–2.06 (6 H, m), 2.49 (3 H, s), 3.44–3.72 (2 H, m), and 3.97–4.28 (2 H, m).

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