

Iron(II) ion-catalysed synthesis of α -aryl and α -alkylthioacetamides

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Abstract

The potential of iron(II)-catalysed reactions the synthesis of α -aryl and α -alkyl thioacetamides from acetylthiomides is reported. Iron(II) ion efficiently catalyses reactions of iodobenzene **1a** or 1-iodoadamantane **1b** with *N*-thioacetylmorpholine anion **2** in DMSO. Ferrous bromide amounts in the 0.6–1.6 mol% range are large enough to reach yields of 86% of α -phenyl-*N*-thioacetylmorpholine **3a** and 65% of α -(1-adamantyl)-*N*-thioacetyl-morpholine **3b**. These catalytic reactions are more easily handled than photoinduced reactions, and provide a useful route to the synthesis of α -aryl and α -alkyl thioacetamides from acetylthiomides without the need for special photochemical devices. A possible reaction pathway is suggested for the iron(II)-catalysed process involving iron-thioamide enolate complexes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thioamides are versatile intermediates that have found wide application in the synthesis of industrial and fine chemical products [1–3]. They are used as vulcanisation accelerators, additives to lubricating oils, corrosion inhibitors, flotation agents, insecticides and fungicides, preservatives, and intermediates for preparation of certain vitamins (e.g. B₁) and other pharmaceutical products [4]. Thioamides have also attracted attention in peptide chemistry [5,6]. Particularly, α -substituted thioacetamides are useful

synthetic intermediates and would provide an alternative route to aryl propionic acids used in the synthesis of non-steroidal anti-inflammatory and analgesic drugs.

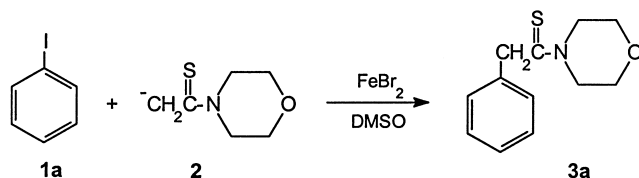
Conventional preparative methods of functionalised thioamides are based upon: (a) reactions of amides with phosphorus pentasulfide, Lawesson's reagent or other sulfurating reagents [7–9]; (b) the Willgeroudt–Kindler reaction [10–13]; and, (c) addition reactions with Grignard reagents [14,15]; among others. Recently, we have reported the preparation of α -aryl and α -alkylthioacetamides by photostimulated and iron(II)-induced nucleophilic substitution reactions [16]. We now extend our previous work to analyse the potentiality of the iron(II)-catalysed synthetic route to produce α -substituted thioacetamides employing catalytic amounts of the ferrous salt.

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Scheme 1.

After Galli and Bunnett's discovery, the successful use of the iron(II) ion to induce substitution reactions by the $S_{RN}1$ mechanism has grown in importance [17,18]. Arylacetic esters or acids, arylacetamides and arylalkanamides were obtained with FeSO_4 /substrate (limiting reactant) molar ratios in the 20–100% range, using liquid ammonia as solvent [19]. The FeCl_2 /substrate molar ratios in the 12–40% range showed to be enough to obtain aryl or heteroaryl ketones in fair to good yields from several aryl and heteroaryl halides with ketone enolate ions in DMSO [20]. Reactions of 7-iodonorcarane, 1-iodoadamantane and neopentyl iodide with acetophenone and 2-naphthyl methyl ketone enolate ions in DMSO were induced with 21–156% FeBr_2 /substrate molar ratios [21]. Also, the efficiency of photo- and iron(II)-induced reactions has been compared for 40% FeCl_2 /substrate molar ratio and several nucleophiles with iodobenzene in DMSO [22]. Recently, reactions of *o*-iodoaniline with aromatic ketones have been induced using a FeBr_2 /substrate molar ratio of 100% in DMSO [23]. In all the contributions that have been mentioned the reactions were induced by the addition of quite more than catalytic amounts of ferrous salts. The evidence available indicates that most, if not all, of the ferrous ion-initiated substitutions are $S_{RN}1$ in nature [16–23]. However, the precise nature of the iron(II) stimulated reactions is not still fully understood [18,20].

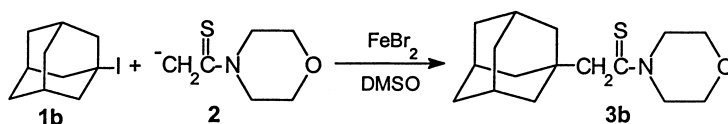
Particularly, the present paper attempts to focus on the synthetic potential of iron(II) catalysis in substitution reactions of iodobenzene **1a** (Scheme 1) and

1-iodoadamantane **1b** (Scheme 2) with the anion of *N*-thioacetylmorpholine **2** as a model nucleophile.

As the following discussion illustrates, the employment of catalytic amounts of the ferrous salt allows us to achieve high yields of α -aryl and α -alkyl thioamides with synthetic advantages. In fact, FeBr_2 /limiting reactant molar ratios up to 20–250 times lower than those previously reported for other iron(II)-induced reactions are sufficient to catalyse the reactions of **1a** or **1b** with **2** in DMSO, which can be more easily handled than photochemical or electrochemical reacting systems.

2. Experimental

Gas-liquid chromatographic (GLC) analyses of the reacting mixture were performed on a Shimadzu GC-17AATF chromatograph equipped with a 3% SE-30 (or 5% OV 17) on Chromosorb P packed column (1.5 m \times 3.1 mm) and flame ionisation detector. Column chromatography was performed on silica gel (70–270 mesh ASTM). On a Büchi 510 micro melting point apparatus mps were determined and were not corrected. Infrared (IR) spectra were recorded on a Nicolet FTIR 5-SXC spectrophotometer; ^1H and ^{13}C NMR spectra on a Bruker FT-200 spectrometer. Mass spectra (MS) were performed on a Finnigan 3300 f-100 spectrometer. Elemental analyses were performed at the Galbraith Laboratories, Inc., Knoxville, United States.



Scheme 2.

2.1. Materials

All reactants were purified according to published procedures before use [24,25]. The DMSO (Carlo Erba) was distilled and dried on molecular sieves (4 Å). High purity anhydrous ferrous bromide (Strem) was used as received and stored under anhydrous atmosphere. Lawesson's reagent was prepared from phosphorous pentasulfide and anisole as previously reported [26]. The *N*-thioacetylmorpholine was prepared from *N*-acetylmorpholine and Lawesson's reagent in HMPA or benzene as solvent [27]. The *N*-acetylmorpholine was also prepared from acetic anhydride and morpholine as described earlier [25]. According to a reported procedure α -(1-Adamantyl)acetophenone was prepared and purified [21], and used as internal standard to perform quantitative GC analyses. Water was double distilled prior to use.

2.2. Typical procedure of catalytic synthesis

Batch reactions were carried out in a 100 ml three-neck round-bottomed flask equipped with reflux apparatus, nitrogen inlet, magnetic stirrer and septum device for the sampling of the reacting mixture during the course of the reaction without stopping the agitation. All reactions of **1a** or **1b** and **2** with *t*-BuOK were carried out in degasified DMSO, under full reflux and inert atmosphere (N₂). Experiments were carried out using catalyst/limiting reactant ratios in the 0.6–2.5 mol% range and substrate/nucleophile molar ratios covering reaction conditions limited by each one of the reactants. The temperatures of the reaction were 323, 337 and 352 K, and kept within ± 1 K.

Liquid samples were withdrawn at different reaction times over a period of 1–4 h, and immediately poured into an excess of ammonium nitrate and double distilled water (25 ml) to stop the reaction. Each sample was extracted three-fold with ethyl ether (3 ml \times 25 ml). The extract was washed with double distilled water until complete elimination of the DMSO for further analysis by GC.

2.3. Catalytic synthesis of α -arylthioacetylammides: α -phenyl-*N*-thioacetylmorpholine **3a**

In 12 ml of DMSO (2.8×10^2 mmol), 204.0 mg (5.3×10^{-1} mmol) of **1a**, 421.1 mg (2.9 mmol) of **2** and

448.9 mg (4.0 mmol) of *t*-BuOK were added. Once the temperature of reaction was achieved, 1.8 mg (8.2×10^{-3} mmol) of ferrous bromide were dissolved stirring vigorously. Zero time was taken when the agitation began. The reacting mixture was treated as described above. By column chromatography on silica gel eluting with petroleum ether–ethyl ether (70:30) and further recrystallisation with ethanol, α -Phenyl-*N*-thioacetylmorpholine **3a** was obtained. Compound **3a** was obtained as a white solid; yield 87%; mp 79–80°C; IR (cm⁻¹) 1112 (s), 1495 (s); ¹H-NMR (200 MHz; CDCl₃; Me₄Si) δ 3.30–3.80 (m, 6H), 4.30 (m, 2H), 4.40 (s, 2H), 7.30 (s, 5H); MS, m/e (relative intensity) 221 (93), 188 (24), 134 (46), 130 (62), 91 (100), 86 (66). Elemental analysis (Calculated for C₁₂H₁₅NOS: C 65.19, H 6.79, O 7.19, N 6.32, S 14.51. Found: C 65.12, H 6.83, O 7.32, N 6.33, S 14.49).

2.4. Catalytic synthesis of α -alkylthioacetylammides: α -(1-adamantyl)-*N*-thioacetyl-morpholine **3b**

In 12 ml of DMSO (2.8×10^2 mmol), 135.8 mg (5.2×10^{-1} mmol) of **1b**, 421.1 mg (2.9 mmol) of **2** and 448.9 mg (4.0 mmol) of *t*-BuOK were added. Then, 1.8 mg (8.2×10^{-3} mmol) of ferrous bromide were quickly dissolved to begin the reaction. The reacting mixture was treated as previously described. Column chromatography on silica gel eluting with petroleum ether–ethyl ether (70:30) and further recrystallisation with ethanol afforded α -(1-adamantyl)-*N*-thioacetylmorpholine **3b** as a white solid; yield 65%; mp 148–149°C; IR (cm⁻¹) 1025.2, 1117.4, 1275.3, 1426.7, 1485.9, 2848.3, 2907.5; ¹H-NMR (200 MHz, CDCl₃; Me₄Si) δ 1.59–1.80 (m, 12H), 1.85–2.12 (m, 3H), 2.85 (s, 2H), 3.66–3.90 (m, 6H), 4.32–4.48 (m, 2H); ¹³C NMR (CDCl₃) δ 28.77, 34.89, 36.64, 43.15, 50.12, 51.56, 55.85, 66.31, 66.56, 200.54; MS, m/e (relative intensity) 279 (53, M⁺), 246 (19), 144 (100), 135 (59), 110 (33), 86 (57). Elemental analysis (Calculated for C₁₆H₂₅NOS: C 69.00, H 8.94, N 5.00, O 5.63, S 11.43. Found: C 68.77, H 9.02, O 5.73, N 5.01, S 11.47).

3. Results and discussion

Reactions of **1a** or **1b** with **2** in DMSO did not occur in the absence of FeBr₂, but yields of **3a** and **3b** up

Table 1

Effect of the ferrous salt loading on the yield of the substitution product **3a**, at 337 ± 1 K

	Substrate 1a (mmol)	Nucleophile 2 (mmol)	FeBr ₂ (mol%)	Yield of substitution product 3a (%)				
				5 min	10 min	20 min	60 min	240 min
1	0.53	2.90	100.00	86	86	87	86	86
2	0.50	3.30	0.56	32	53	62	69	86
3	0.50	3.30	1.60	50	67	76	79	87
4	0.50	3.00	2.50	77	78	80	82	86

to 87 and 64%, respectively, were reached in the presence of catalytic amounts of FeBr₂. Our results show that ferrous bromide amounts as low as 0.6–2.5 mol%, rather than the 100 mol% as reported earlier [16] are large enough to reach the same yields. We attribute it to an efficient catalytic activity of the iron(II) which is apparent from the following evidences.

3.1. Effect of the FeBr₂ loading on the substitution product yields

In dark, small amounts of FeBr₂ give an efficient conversion of **1a** to **3a** under conditions at which the process is otherwise infinitesimally slow. Our experimental data are summarised in Table 1. A 86% yield of **3a** was quickly achieved when the reaction was carried out using a FeBr₂/substrate **1a** ratio of 100 mol% (entry 1). A similar yield was reported earlier [16]. However, we have found that FeBr₂ amounts as low as 0.56–2.50 mol% are large enough to reach the same yield (entries 2–4). These small amounts are typically catalytic and 20–250 times lower than those previously reported for iron(II)-induced substitution reactions which take place by electron transfer (ET), as referenced in the introduction [16–23]. An

additional evidence that suggests the catalytic activity of the iron(II) ion is apparent from the fact that the FeBr₂ loading affects the rate of reaction but does not change the ultimate yield. A similar behaviour was corroborated for the catalytic conversion of **1b** yielding to 65% of **3b** whatever the FeBr₂ loading.

3.2. Effect of the FeBr₂ loading on the rate of reaction

Taking into account the catalytic effect so far exhibited by the iron(II) ion, we have attempted to provide a measure of the degree of efficiency upon the observed catalytic activity. To this purpose, initial rates of reaction were carefully obtained from experimental data of the product distribution in time, for FeBr₂/substrate ratios in the 0.56–2.50 mol% range. A comparison of the effects on the appearance rate of **3a** is shown in Table 2. It is noticeable that when the FeBr₂/substrate molar ratio increases 2.86- and 4.46-folds, the initial reaction rate increases 2.67- and 4.73-folds, respectively (entries 2 and 3). The same linear trend was observed for the appearance rate of **3b**. This ability of iron(II) to proportionally enhance the rate of reaction without being appreciably consumed in the process is another clear evidence of its catalytic activity.

Table 2

Effect of the ferrous salt on the appearance rate of **3a** in DMSO^a

FeBr ₂ (mmol)	FeBr ₂ (mol%)	Rate of appearance of 3a (M s ⁻¹)	Yield of 3a (%)	Rate ratio ^b	FeBr ₂ ratio ^b
2.8×10^{-3}	0.56	3.02×10^{-5}	68 ^c	1.00	1.00
8.0×10^{-3}	1.60	8.06×10^{-5}	71 ^c	2.67	2.86
12.5×10^{-3}	2.50	1.43×10^{-4}	81 ^d	4.73	4.46

^a Reactions of **1a** (0.5 mmol) and **2** (3.3 mmol) were carried out in a DMSO solution (282 mmol), at 323 K.

^b Relative value to 0.56 mol% ratio.

^c At 60 min.

^d At 70 min.

3.3. Effect of the temperature on the rate of reaction

The observed rate of appearance of the substitution products **3a** and **3b** triples itself for a 10 K rise in temperature. For example, the values of the rate constant were $2.69 \pm 0.34 \times 10^{-2}$ and $2.47 \pm 0.33 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ at 323 and 352 K, respectively, for the rate of reaction between **1a** and **2** using a 0.56% FeBr_2 /substrate molar ratio. Similar reactivities have been reported for aromatic nucleophilic substitution reactions of *p*-halonitrobenzene with nucleophiles in DMSO [28,29]. According to the Arrhenius relationship, the estimated activation energy was $17,205 \pm 2018 \text{ cal mol}^{-1}$ (72% confidence limit).

3.4. Product distribution

Typical concentration profiles from iron(II)-catalysed reaction of **1a** and **2** in DMSO are shown in

Fig. 1. By inspection of these profiles, the following points may be highlighted:

1. The limiting reactant becomes almost depleted in the process even when relative small amounts of FeBr_2 were used, as shown in Fig. 1a. Therefore, there is no stoichiometric relationship between the observed changes in the FeBr_2 /reagent molar ratios and the overall stoichiometry of the substitution reactions as expected for a catalytic process.
2. A careful examination of Fig. 1b and c reveals that the nucleophile and substrate concentrations affect the disappearance rate of **1a** and the appearance rate of **3a**. In order to provide quantitative information, we have estimated the order of reaction from controlled experiments. Concentrations of both reactants were independently changed to obtain a better quantification of their influence on the measured rate of reaction, which is overall second-order, being first-order in **1a** and first-order

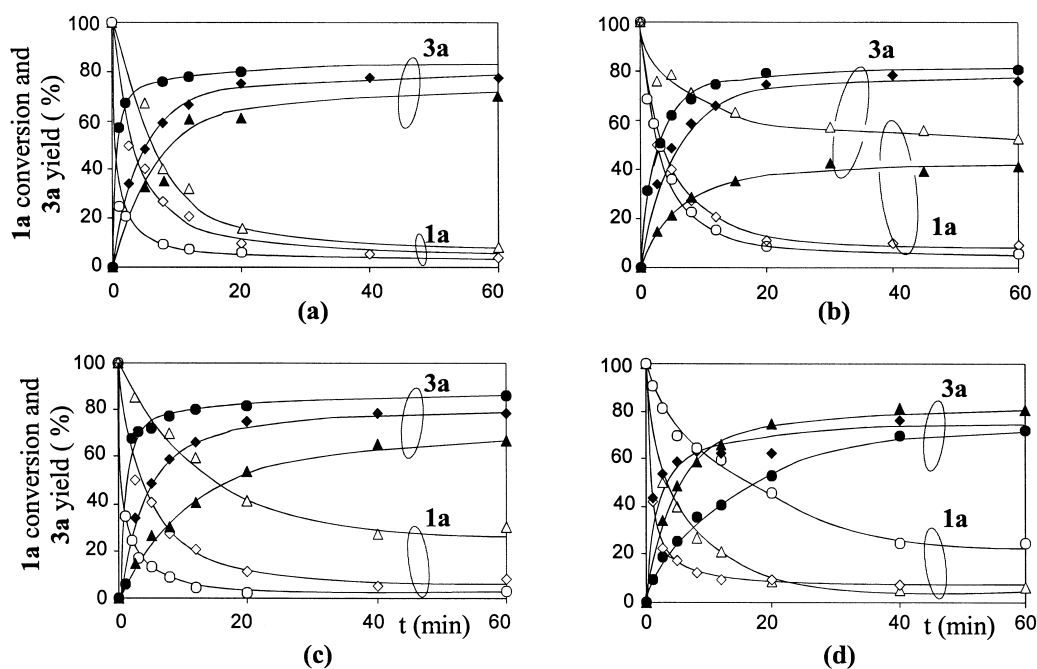
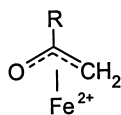


Fig. 1. Conversion of iodobenzene (**1a**) and yield of α -phenyl-*N*-thioacetylmorpholine (**3a**) as a function of the reaction time. (a) Effect of the ferrous bromide amount: (▲) 0.6 mol%, (◆) 1.6 mol%, and (●) 2.5 mol%, for 0.5 mmol of **1a** and 3.3 mmol of **2**. (b) Effect of the nucleophile concentration: (▲) 0.3 mmol, (◆) 3.3 mmol and (●) 5.0 mmol, for 0.5 mmol of **1a** and 1.6 mol% of ferrous bromide. (c) Effect of the substrate concentration: (▲) 0.15 mmol, (◆) 1.6 mmol, and (●) 2.0 mmol for 3.0 mmol of **2** and 1.6 mol% of ferrous bromide. (d) Effect of the temperature of reaction: (●) $223 \pm 1 \text{ K}$, (◆) $337 \pm 1 \text{ K}$, and (▲) $252 \pm 1 \text{ K}$, for 0.5 mmol of **1a**, 3.0 mmol of **2** and 1.6 mol% of ferrous bromide.



Scheme 3.

in **2**. The same functionality was found for the reaction rate of **1b** and **2**. Although the order of reaction certainly coincides with the molecularity only for elementary processes, the overall second-order reaction suggests that unimolecular mechanisms are less probable than bimolecular ones.

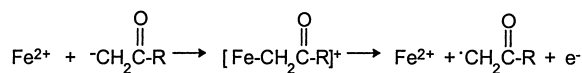
- An increase of the temperature above 337 K decreases the selectivity towards the substitution product **3a**. A similar behaviour was observed for **3b**. Therefore, if an increase of the rate of reaction is desired above that temperature, an increase of the catalyst loading rather than the temperature of the reaction is recommended (Fig. 1d).

3.5. Mechanistic considerations

In connection with the intermediacy of the iron(II) ion into the catalytic process, the involvement of an iron-ketone enolate complex has been postulated to explain iron(II)-catalysed reactions between aryl and heteroaryl halides with ketone enolate anions in DMSO (Scheme 3) [22]. This interpretation was supported by IR analysis [22] and suggested from the observance of a strong darkening of the nucleophile solution after addition of the ferrous salt [19,22].

This iron-ketone enolate complex combines with the substrate yielding an intermediate complex which enhances the feasibility of the ET from the enolate anion to substrate, as shown in Scheme 4 [22].

On the other hand, an analogous mechanism suggests that the iron-ketone enolate complex would undergo decomposition to give a ketyl-like enolate, the



Scheme 5.

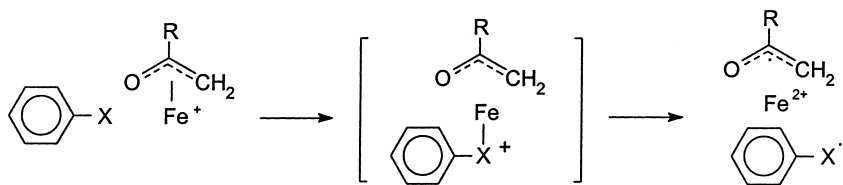
iron(II) ion and an electron which can then be transferred to the substrate (Scheme 5) [19].

Whatever the mechanism, the iron(II) ion is restored into the cyclic process. However, some aspects of the intermediacy of the iron(II) ion remain still understood for systems involving the ketone functionality. Certainly, even less is known about complexes with the thioamide functionality.

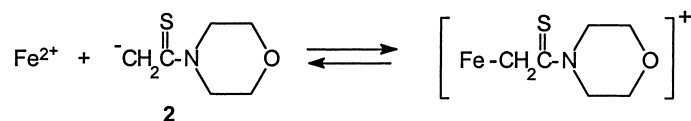
Regarding the formation of an iron-organo complex involving the thioamide enolate of the *N*-thioacetylmorpholine **2**, infrared observation reveals that the addition of *t*-BuOK to the DMSO solution of **2** causes the appearance of an absorption band at 1637 cm^{-1} , probably due to the formation of the thioamide enolate. This absorption band does not disappear after the addition of FeBr_2 amounts up to seven-fold greater than the stoichiometric ratio. However, a rapid darkening of the solution of **2** in DMSO that takes place with the addition of FeBr_2 appears to be indicative of the formation of an iron-thioamide enolate complex like those involved in iron(II) ion and ketone enolate systems. We attribute the lack of a whole disappearance of that absorption band as being due to the formation of a complex of reversible nature, as shown in Scheme 6.

A further decomposition of the complex would restore the iron(II) ion and lead to a thioamide-like enolate and an electron, as shown in Scheme 7. The electron can be transferred to substrate, **1a** or **1b**, by ET as suggested for other reacting systems [19].

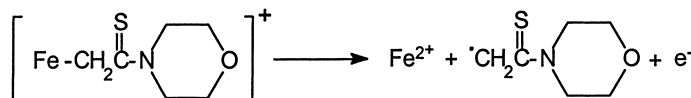
A simple deduction of the overall kinetic equation based on Schemes 6 and 7 confirms that there is good agreement between the proposed sequence, involving



Scheme 4.



Scheme 6.



Scheme 7.

a reversible step to the formation of the complex, and the observed overall second-order reaction. Therefore, the proposed sequence would be a probable pathway; however, the intimate mechanism remains to be clarified. Further experiments to analyse the effect of the iron(II) on the redox potential of the thioamide enolate anion are currently in progress to gain a better understanding.

In order to explain the apparent need for lower concentrations of Br_2Fe to catalyse reacting systems involving nucleophiles with thioamide functionality rather than ketone, we are inclined to attribute it to a faster decomposition of the iron-thioamide enolate complex than the iron-ketone enolate complex. The bigger size and the lower electronegativity of the sulphur atom than the oxygen atom ones, would be factors capable of enhancing the rate of decomposition of the iron-thioamide enolate complex leading to a more efficient catalytic route.

4. Conclusions

Experimental evidence was provided to show the potential of iron(II)-catalysed reactions to the synthesis of α -aryl and α -alkyl thioacetylammides from acetylthiomides. Our results indicate that ferrous bromide amounts as low as 0.6–2.5 mol% are large enough to reach high yields of the substitution products **3a** and **3b**. Yields of **3a** higher than 80% can be obtained by the employment of a FeBr_2 loading comprised in the mentioned range, when the nucleophile is a non-limiting reagent, the substrate concentration is $>5 \times 10^{-2}$ M, and the temperature of reaction does

not exceed 337 K. Yields of **3b** >65% can be obtained under the same conditions.

It can then be concluded that all these results indicate that the iron(II) ion efficiently catalyses nucleophilic substitution reactions on inactivated aromatic rings and bridgehead alkyl substrates, and that it appears to be definitely more efficient than those reported for acetylammides. The catalytic reactions here reported are more easily handled than photoinduced reactions, and provide a useful route to the synthesis of α -aryl and α -alkyl thioacetylammides from acetylthiomides without the need for special photochemical devices.

Acknowledgements

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