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MECHANISM OF BIMOLECULAR SUBSTITUTION REACTIONS OF HYDROXIMOYL HALIDES WITH AMINES IN ACTONITRILE SOLUTION

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The reaction in acetonitrile solution of (*Z*)-*O*-methylbenzohydroximoyl chlorides [ArC(Cl)=NOCH$_3$] with morpholine, pyrrolidine and azetidine gives the corresponding (*Z*)-amidoximes [ArC(NR^{1}R^2)=NOCH$_3$] in acetonitrile. The rates of these reactions were measured under pseudo-first-order conditions (excess amine). The reactions were found to follow overall second-order kinetics (first order in amine). The Hammett ρ-value (with σ) for the reaction with pyrrolidine is +0·92. The reaction of the *p*-nitro compound with pyrrolidine gives a significant element effect [k(*p*-nitrobenzohydroximoyl bromide)/k(*p*-nitrobenzohydroximoyl chloride = 10]. A Brønsted β-value of 0·38 was estimated from the reactions of morpholine and piperidine with the *p*-nitrohydroximoyl chloride. The slower reaction of (*E*)-*O*-methyl-*p*-nitrobenzohydroximoyl chloride with azetidine gives primarily the (*E*)-amidoxime ($E:Z \approx 98:2$) This reaction also follows second-order kinetics. The kinetic observations made in this study are compared with the corresponding results obtained in earlier work in benzene solution. It is suggested that in acetonitrile solution the reactions proceed by an addition–elimination mechanism with rate-determining loss of chloride ion ($A_N + D_{N\#}$). It is further suggested that acetonitrile is assisting in the breakdown of the tetrahedral intermediates formed in these reactions.

1. INTRODUCTION

The kinetics and stereochemistry of nucleophilic substitution reactions of secondary cyclic amines (morpholine, piperidine, pyrrolidine and azetidine) with (*Z*)-*O*-methylbenzohydroximoyl chlorides (**1Z**) in benzene solution has been reported.[1,2] The kinetic equations for these reactions contained second-order (first order in **1Z** and first order in amine) and third-order (first order in **1Z** and second order in amine) terms:

$$k_{obs}\ (\text{l mol}^{-1}\,\text{s}^{-1}) = k''[\text{amine}] + k'''[\text{amine}]^2$$

The third-order rate constants gave a positive Hammett ρ-value (+1·06 with pyrrolidine[1] and ca +1·0 with azetidine[2]) whereas the second-order rate constants showed no systematic substituent effect. A substantial element effect was observed on both the second- and third-order rate constants. It was suggested that these reactions proceed by an addition–elimination mechanism with the rate-determining step being the loss of chloride ion from the tetrahedral intermediate. It was further suggested that the amine-catalyzed pathway involved deprotonation of the zwitterionic tetrahedral intermediate (**T-1** in Scheme 1) by an amine molecule (**TS-2**). In the transition state for the deprotonation, some of the positive charge is removed from the tetrahedral intermediate to the amine molecule, leaving a disproportionate amount of negative charge near the aromatic ring. In the second-order pathway the transition state (**TS-1**) for unassisted elimination of the chloride ion would have approximately the same amount of negative and positive charge near the aromatic ring. It was argued that the third-order pathway should give a positive Hammett ρ-value while there should not be a substituent effect on the second-order process.

The slower reaction of azetidine with the (*E*)-hydroximoyl chloride **1Ea** in benzene gave a mixture of the (*E*)- and (*Z*)-amidoximes (**2Ei** and **2Zi**) with the *E* isomer predominating ($E:Z = 98:2$). The rate equation for this reaction contained first- and third-order terms in azetidine:

$$k_{obs}\ (\text{l mol}^{-1}\,\text{s}^{-1}) = k''[\text{azetidine}] + k'''[\text{azetidine}]^3$$

It was suggested that the amine-catalyzed reaction involved nucleophilic attack by an amine monomer to form a tetrahedral intermediate (**T-2** in Scheme 2),

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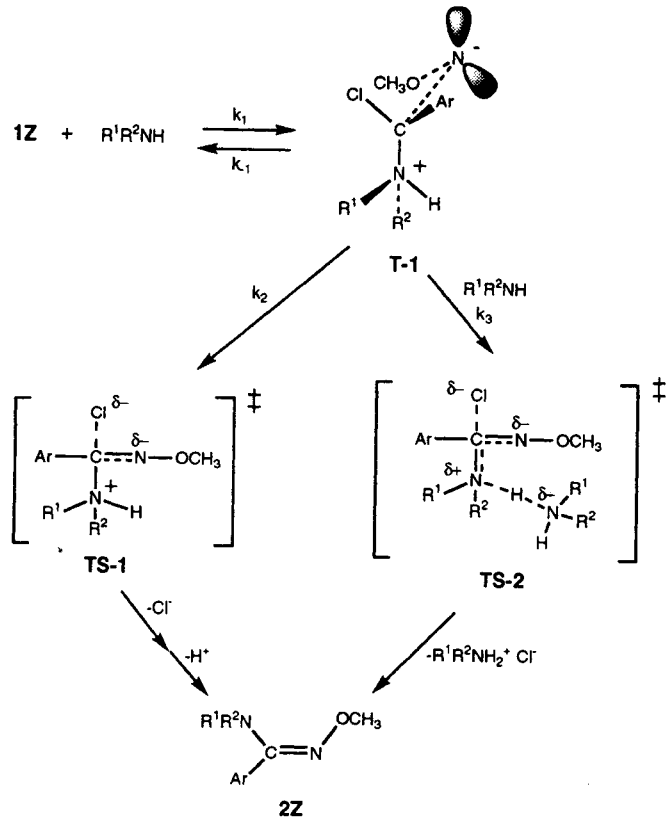
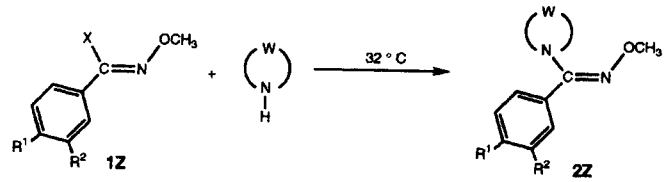
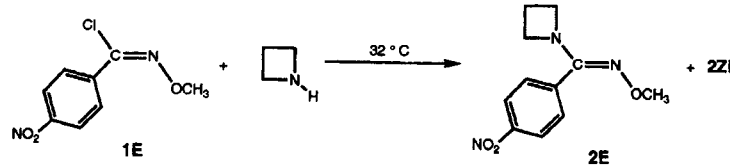


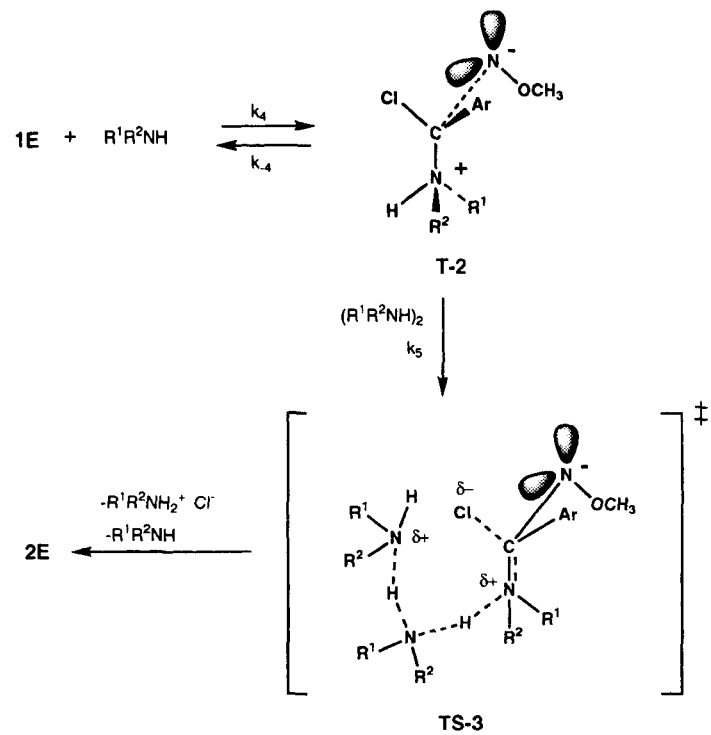
Scheme 1



1Za: X = Cl; $R^1 = NO_2$; R^2 = H
b: X = R^1 = Cl; R^2 = H
c: X = R^2 = Cl; R^1 = H
d: X = Cl; $R^1 = R^2$ = H
e: X = Cl; $R^1 = CH_3$; R^2 = H
f: X = Cl; R^1 = t-C_4H_9; R^2 = H
g: X = Br; $R^1 = NO_2$; R^2 = H

2Za: $R^1 = NO_2$; R2 = H W = $(CH_2)_4$
b: R^1 = Cl; R^2 = H; W = $(CH_2)_4$
c: R^1 = H; R^2 = Cl W = $(CH_2)_4$
d: $R^1 = R^2$ = H; W = $(CH_2)_4$
e: $R^1 = CH_3$; R^2 = Cl; W = $(CH_2)_4$
f: R^1 = t-C_4H_9; R^2 = H; W = $(CH_2)_4$
g: $R^1 = NO_2$; R^2 = H; W = $(CH_2)_5$
h: $R^1 = NO_2$; R^2 = H; W = $(CH_2)_2O(CH_2)_2$
i: $R^1 = NO_2$; R^2 = H; W = $(CH_2)_3$
j: R^1 = Cl; R^2 = H; W = $(CH_2)_3$
k: $R^1 = R^2$ = H; W = $(CH_2)_3$





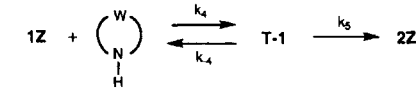
Scheme 2

which broke down with the assistance of an amine dimer. The amine dimer deprotonates the ammonium ion nitrogen of the tetrahedral intermediate and at the same time assists in the departure of the nucleofuge (**TS-3**). In our view, the additional assistance is required in the tetrahedral intermediate **T-2** because there are no electron pairs antiperiplanar to the nucleofuge (compare tetrahedral intermediate **T-1** derived from **1Z** with tetrahedral intermediate **T-2** derived from **1E**).

RESULTS AND DISCUSSION

In this work, the substitution reactions of *O*-methylbenzohydroximoyl chlorides (**1Z**) with secondary cyclic amines were investigated with acetonitrile as the solvent for the reactions. In all the reactions studied the (*Z*)-hydroximoyl chlorides (**1Z**) gave only the *Z* substitution products (amidoximes, **2Z**). The rate constants (Table 1) for these reactions were measured under pseudo-first-order conditions (excess amine). The second-order rate constants for the reactions of **1Z** with amines in acetonitrile do not increase significantly with increasing amine concentration. Thus the third-order term that was found in benzene solution has disappeared in acetonitrile solution.

A significant element effect was observed for the reaction of (*Z*)-*p*-nitrobenzohydroximoyl halides (**1Za** and **1Zg**) with pyrrolidine; the rate constant for the hydroximoyl bromide **1Zg** is about 10 times larger than that for the hydroximoyl chloride **1Za**. This observation is consistent with rate determining elimination of halide ion from the tetrahedral intermediate. It is possible, however, that nucleophilic attack on the hydroximoyl chloride by the amine is rate determining. Application of the steady-state treatment to an addition–elimination



mechanism gives the following for the observed second-order rate constant (k''):

$$k'' = \frac{k_4 k_5}{k_{-4} + k_5}$$

Only in the case where $k_5 \gg k_{-4}$ does k_5 cancel out and a negligible element effect would be expected. In the case where k_{-4} is greater than k_5 or where $k_{-4} \approx k_5$, an element effect would be expected for the reaction. In the present case, we assume that k_{-4} is greater than k_5. This assumption is based on kinetic measurements[3] that

Table 1. Pseudo-first-order rate constants (k') and second-order rate constants (k'') for the reactions of (*Z*)- and (*E*)-*O*-methylbenzohydroximoyl chlorides with secondary cyclic amines in acetonitrile at 32·0 °C

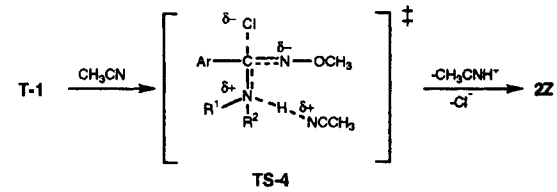
No.	Amine	[Amine] (M)	$10^5 k'$ (s^{-1})	$10^5 k''$ (l mol^{-1})
1Za	Pyrrolidine	1·00	6·66	6·66
1Za	Pyrrolidine	1·25	6·39	5·11
1Za	Pyrrolidine	1·50	10·4	6·93
1Zb	Pyrrolidine	1·00	3·00	3·00
1Zb	Pyrrolidine	1·25	3·92	3·14
1Zb	Pyrrolidine	1·50	4·87	3·24
1Zb	Pyrrolidine	1·75	5·52	3·15
1Zc	Pyrrolidine	1·00	3·98	3·98
1Zc	Pyrrolidine	1·25	5·47	4·37
1Zc	Pyrrolidine	1·50	6·80	4·53
1Zd	Pyrrolidine	0·87	1·52	1·75
1Zd	Pyrrolidine	1·50	2·89	1·93
1Zd	Pyrrolidine	1·75	3·49	1·99
1Ze	Pyrrolidine	1·00	0·960	0·960
1Ze	Pyrrolidine	1·25	1·25	1·00
1Ze	Pyrrolidine	1·50	1·41	0·940
1Zf	Pyrrolidine	1·25	1·35	1·08
1Zf	Pyrrolidine	1·50	1·61	1·07
1Zf	Pyrrolidine	1·75	1·91	1·09
1Za	Piperidine	0·50	0·382	0·760
1Za	Piperidine	1·00	0·826	0·83
1Za	Piperidine	2·00	1·83	0·92
1Za	Piperidine	2·50	2·52	1·01
1Za	Piperidine	3·00	3·08	1·03
1Za	Morpholine	1·25	0·083	0·064
1Za	Morpholine	1·50	0·104	0·069
1Za	Morpholine	1·75	0·134	0·077
1Za	Morpholine	2·00	0·159	0·079
1Za	Azetidine	0·30	6·12	20·4
1Za	Azetidine	0·50	10·7	21·4
1Za	Azetidine	1·00	23·0	23·0
1Za	Azetidine	1·50	38·1	25·4
1Za	Azetidine	2·00	56·4	28·2
1Zb	Azetidine	0·50	5·83	11·7
1Zb	Azetidine	0·75	8·88	11·8
1Zb	Azetidine	1·25	16·6	13·2
1Zb	Azetidine	1·50	20·3	13·6
1Zb	Azetidine	2·00	29·3	14·6
1Zd	Azetidine	1·25	7·57	6·06
1Zd	Azetidine	1·75	10·8	6·17
1Zd	Azetidine	2·00	12·2	6·10
1Zd	Azetidine	2·25	13·8	6·12
1Zg	Azetidine	0·50	97·0	194
1Zg	Azetidine	0·75	151	202
1Zg	Azetidine	1·00	217	230
1Zg	Azetidine	1·25	288	230
1Zg	Azetidine	1·50	366	243
1Ea	Azetidine	0·50	0·242	0·484
1Ea	Azetidine	0·75	0·317	0·423
1Ea	Azetidine	1·00	0·450	0·450
1Ea	Azetidine	1·50	0·721	0·470

show that amines are better nucleofuges than chloride ion in alkene-forming elimination reactions by a factor of at least 20.

The rate constant for the reaction of (*Z*)-*p*-nitrohydroximoyl chloride (**1Za**) with piperidine is substantially larger than the reaction with morpholine. Since the steric requirements are about the same for these two amines, we have estimated the Brønsted β-value for this reaction to be 0·38. This is close to the β-values obtained by us in benzene solution.[2] Ta-Shma and Rappoport[4] reported Brønsted β-values of 0·22–0·48 for reactions that proceeded by addition–elimination, but much smaller values when the reaction involved nitrilium ion formation ($\beta = 0{\cdot}028$).

The substituent effect on the reaction of **1Z** was investigated for pyrrolidine (six points) and azetidine (three points). In contrast to the reaction in benzene solution, a significant substituent effect was observed on the second-order rate constants. The Hammett ρ-value for **1Z** with pyrrolidine is +0·92 (with σ, $r = 0{\cdot}966$) and the estimated ρ-value with azetidine is +0·70. Since the second-order process in benzene solution showed no substituent effect, we suggest that a molecule of acetonitrile is assisting in the deprotonation of the tetrahedral intermediate (**TS-4**). There is a precedent for this suggestion in a recent report by Kevill and Knauss[5] on the mechanism of methanolysis of aromatic acyl bromides; they reported general-base catalysis by either methanol or acetonitrile in the breakdown of tetrahedral intermediates formed in these reactions.

The reaction of **1Ea** with azetidine also proceeds with retention of configuration to give primarily the (*E*)-amidoxime (**2Ei**:**2Zi** ≈ 98:2). It is noteworthy that



TS-4

the complicated kinetic behavior observed for the reaction of **1Ea** with azetidine in benzene solution disappears in acetonitrile; no systematic increase in the second-order rate constant was observed on increasing the amine concentration (Table 1). Further, the rate constants for both the the (*Z*)- and (*E*)-hydroximoyl chlorides **1Za** and **1Ea** increased in acetonitrile as compared with benzene, but the solvent effect is greater on the *E* than the *Z* isomer. In acetonitrile at 1·00 M azetidine the k'(**1Za**):k'(**1E**) ratio is 51 as compared with a k'(**1Za**):k'(**1E**) ratio of 160 in benzene solution.

We suggest in the reaction of **1Ea** with azetidine in acetonitrile that one acetonitrile molecule is assisting in deprotonating the ammonium ion nitrogen. Since acetonitrile is the solvent for the reaction, this assistance is likely to be more efficient than the assistance provided by an amine dimer in benzene solution; consequently the difference in rate constants between the *Z* and *E* isomers is smaller in acetonitrile than in benzene solution.

Table 2 contains a summary of the results obtained from mechanistic probes used in this research as compared with the results obtained on some other nucleophilic substitution reactions on the carbon–nitrogen double bond. In our view, these results present fairly convincing evidence for the mechanisms

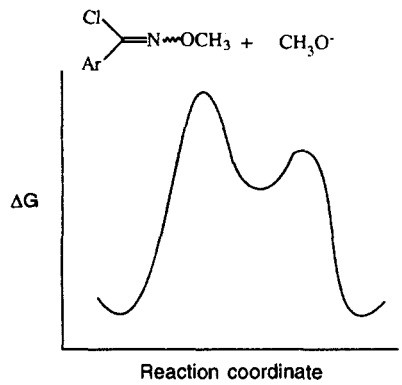
Table 2. Comparison of Hammett ρ-values, Brønsted β-values and element effects for nucleophilic substitution reactions at the carbon–nitrogen double bond

	1Z + amines in acetonitrile (this work)	**1Z** + amines in benzene (Refs 1 and 2)	**1Z** + methoxide in DMSO–methanol (Ref. 6)	Imidoyl chlorides + amines in benzene[a] (Ref. 4)	**1Z** + water in water–dioxane (Ref. 8)	Imidoyl chlorides + amines in benzene[b] (Ref. 4)
Mechanism[c]	$A_N + D_{N\#}$	$A_N + D_{N\#}$	$A_{N\#} + D_N$	$A_{N\#} + D_N$	$D_{N\#} + A_N$	$D_{Nint} + A_{N\#}$
Hammett ρ-values	0·92 (σ)	0 (k'') 1·0 (σ, k''')	1·9 (σ)	1·7–2·6 (σ)	−2·4 (σ^+)	−1·0 (σ^+)
Brønsted β-values	0·38	0·35 (k'') 0·38 (k''')	—	0·22 – 0·48	—	0·028
Element effect (k_{Br}/k_{Cl})	10	11·9 (k'') 8·16 (k''')	2·1	—	41	440

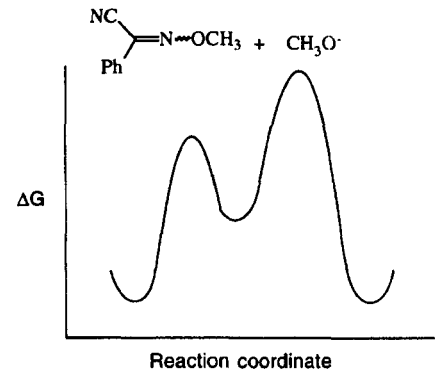
[a] For electron-attracting groups.
[b] For electron-donating groups. [c] Described by the IUPAC system (Refs. 6 and 7).

proposed in this work and in our earlier work on nucleophilic substitution at the carbon–nitrogen double bond.

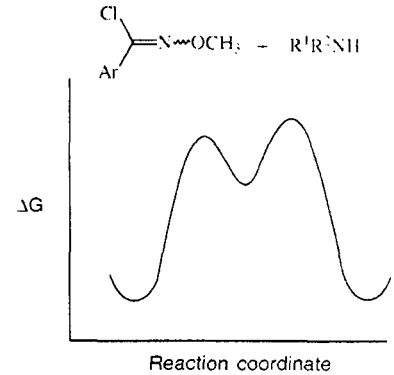
Nucleophilic substitution on hydroximoyl chlorides with a weak nucleophile (H_2O) proceeds by rate-determining ionization to a nitrilium ion[8] ($D_{N\#} + A_N$; Table 2). With a much better nucleophile, methoxide ion, the reaction proceeds by rate-determining nucleophilic attack to form a short-lived tetrahedral intermediate[9] (Reaction Coordinate Diagram 1). The short lifetime of the tetrahedral intermediate permits the tetrahedral intermediate to maintain its stereochemical integrity. In more recent work[10] we have found that stereomutation of the tetrahedral intermediate takes place during methoxide ion substitution on hydroximoyl cyanides [PhC(CN)=NOCH$_3$]. Stereomutation is evidenced by isomerization of the starting material ($E \rightarrow Z$) during the course of substitution. The rate-determining step in this substitution reaction is loss of a poor nucleofuge, cyanide ion, from the tetrahedral intermediate ($A_N + D_{N\#}$). In this reaction the tetrahedral intermediate has a long enough lifetime to undergo C–N bond rotation before elimination of either methoxide ion or cyanide ion can take place, i.e. the energy minimum for the tetrahedral intermediate in this reaction is lower with respect to the transition states for elimination (Reaction Coordinate Diagram 2) than in the reaction of hydroximoyl chlorides with methoxide ion (Reaction Coordinate Diagram 1). In the reactions of secondary amines with hydroximoyl chlorides[1,2] the tetrahedral intermediates have short lifetimes. Since protonated amines are excellent nucleofuges,[3] the loss of the attacking amine is reversible and the rate-determining step is elimination of chloride ion ($A_N + D_{N\#}$; Reaction Coordinate Diagram 3). The short lifetime of the intermediate in these reactions is due to the rapid loss of the attacking amine; the tetrahedral intermediate reverts to starting materials at a faster rate than stereomutation takes place.



Reaction Coordinate Diagram 1



Reaction Coordinate Diagram 2



Reaction Coordinate Diagram 3

EXPERIMENTAL

General methods. The acetonitrile was purchased from Burdick and Jackson and was stored over 3 A molecular sieves. The hydroximoyl halides (**1Za**, **b**, and **d–g**) and the amine substitution products have been reported previously. The preparation of the hydroximoyl chloride **1Zc** and its pyrrolidine substitution product **2Zc** are described in this section. Melting points were carried out using a Thomas–Hoover Unimelt capillary melting point apparatus and are uncorrected. Preparative GLC was carried out with a column (30 ft × 0·375 in. i.d.) of silicone gum rubber (SE-30) on 45–60-mesh Chromosorb W. Elemental analyses were performed at Atlantic Microlab (Norcross, GA, USA) and Midwest Microlab (Indianapolis, IN, USA). ^{1}H-NMR spectra were determined using a Varian EM-390 spectrometer (90 MHz) and infrared spectra with a Midac FTIR spectrophotometer. Low-resolution mass spectra were obtained using a Varian Saturn 3 ion trap GC–mass spectrometer.

Product distributions. The distribution of products in the reactions of **1Za–g** and **1Ea** with cyclic amines

were determined using an HPLC method described previously.[2]

Kinetic method. The general procedure for preparation and thermostating the hydroximoyl chloride–amine solutions has been described previously.[1,2] The reactions were followed by ultraviolet spectrophotometry. The amines (pyrrolidine, morpholine, piperidine and azetidine) were purchased from Aldrich Chemical. The kinetic runs were carried out using freshly distilled amines.

Methyl m-*chlorobenzohydroxamate.* Dimethyl sulfate (11·65 g) was added to a water (100 ml) solution of potassium *m*-chlorobenzohydroxamate (9·69 g, prepared from ethyl *m*-chlorobenzoate and hydroxylamine[11]) and potassium hydroxide (7·74 g). The solution was heated (46 °C) and stirred for 19 h, after which time it did not give a purple color with alcoholic iron (III) chloride solution. The solution was cooled in an ice-bath and carefully acidified with cold concentrated hydrochloric acid. The crystals (6·77 g, 79%) which formed were filtered and dried, m.p.110–111 °C. Several recrystallizations from methanol–water solution gave colorless crystals, m.p 118–119 °C; IR (Nujol), 3139 (N-H), 1656 (C=O, 1568, 1516 cm^{-1}; NMR (DMSO-d_6), δ 3·60 (singlet, NH,1H), 3·80 (singlet, CH_3, 3H), 7·32–8·00 (m, aromatic H, 4H); analysis, calculated for $C_8H_8NO_2Cl$, C 51·77, H 4·34, N 7·55, Cl 19·10; found, C 51·73, H 4·20, N 7·51, Cl 18·76%.

(Z)-O-*Methyl*-m-*chlorobenzohydroximoyl chloride* (**1Zc**). Phosphorus pentachloride (4·46 g) was slowly added with stirring to methyl *m*-chlorobenzohydroxamate (4·00 g) in a 100 ml round-bottomed flask cooled in an ice-bath. The flask was allowed to warm to room temperature and was then heated at 65 °C for 20 h. The flask was cooled to room temperature and the liquid product was poured slowly with stirring into cold water. The resulting mixture was extracted several times with chloroform. The combined chloroform extracts were washed with 10% silver nitrate solution, water, 10% sodium hydrogencarbonate solution, water, sodium hydroxide solution (6 M) and water. The chloroform solution was dried and the chloroform was removed by evaporation at aspirator pressure. The residual oil was distilled to give a colorless oil (1·75 g, 39%), b.p. 84–85 °C (0·7 Torr); IR (neat), 1595, 1584, 1560 (C=N) cm^{-1}; NMR ($CDCl_3$), δ 4·10 (s, CH_3, 3H), 7·39 (m, aromatic H, 2H), 7·82 (m, aromatic H, 2H); MS, *m/z* (relative intensity, %), 207 (9·9, $M^+ + 4$), 205 (59, $M^+ + 2$), 203 (91, M^+), 170 (26), 168 (85), 155 (31), 153 (100), 139 (17), 137 (48), 113 (9·6), 111 (25), 75 (49); analysis, calculated for $C_8H_7NOCl_2$, C 47·09; H 3·46; N 6·86, Cl 34·75; found, C 47·28, H 3·49, N 6·83, Cl 34·64%.

(Z)-O-*Methyl pyrrolidino*-m-*chlorobenamidoxime* (**2Zc**). (*Z*)-*O*-Methyl-*m*-chlorobenzohydroximoyl chloride (1·00 g, 0·05 mol) and pyrrolidine (7·10 g, 0·101 mol) were placed in a round-bottomed flask and stirred with a magnetic stirring bar for 48 h at room temperature in the dark. Diethyl ether (150 ml) and ice (50 g) were added and the mixture was stirred vigorously for 5 min. The ether layer was separated and washed with cold water (2 × 20 ml). The ether layer was dried over anhydrous magnesium sulfate and the ether was removed under aspirator pressure. The remaining ether was removed from the residual oil by reducing the pressure inside the flask to 0·20 Torr for 1 h at room temperature. A light-yellow oil (1·02 g, 85%) was obtained: ^1H NMR ($CDCl_3$), δ 1·80 (m, CH_2CH_2, 4H), 3·40 [*t*, $N(CH_2)_2$, $J = 7·5$ Hz, 4H], 3·72 (s, CH_3, 3H), 7·35 (m, aromatic H, 4H); MS, *m/z* (relative intensity, %), thermal isomerization (*Z* to *E*) in the gas chromatograph produced two peaks in the mass chromatogram with identical mass spectra, 240 (4·9, $M^+ + 2$), 238 (16·9, M^+),138 (16·5), 70 (100); IR (neat), 1603,1594 cm^{-1}; analysis, calculated for $C_{12}H_{15}N_2OCl$, C 60·38, H 6·33, N 11·73, Cl 14·85; found, C 60·24; H 6·38, N, 11·65, Cl 14·75%.

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