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STEREOCHEMISTRY AND KINETICS OF METHOXIDE ION SUBSTITUTION IN (*Z*)- AND (*E*)-*O*-METHYLBENZOHYDROXIMOYL CYANIDES

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The stereochemistry and kinetics of the methoxide ion substitution reactions (Z)- and (E)-methylbenzohydroximoyl cyanide [PhC(CN)=NOCH$_3$] were investigated. The reaction of the (Z)-hydroximoyl cyanide with sodium methoxide in DMSO–methanol (9:1) solution at 44·8 °C gives a mixture of methyl (Z)-O-methylbenzohydroximate [PhC(OCH$_3$)=NOCH$_3$] and the O-methyloxime of α-ketophenylacetamide [PhC(CONH$_2$)=NOCH$_3$). The (E)-hydroximoyl cyanide undergoes methoxide ion-catalyzed isomerization to the E-isomer faster than it undergoes nucleophilic substitution. These observations were interpreted in terms of an addition–elimination mechanism in which the rate-limiting step is elimination of the nucleofuge ($A_N + D_{N\#}$).

INTRODUCTION

In basic or neutral solution, nucleophilic substitution at the carbon–nitrogen double bond[1–10] has been shown to proceed by pathways A and B outlined in Scheme 1. In pathway A, the nucleophile adds to the carbon–nitrogen double bond to give a tetrahedral intermediate which undergoes elimination of the nucleofuge (described by the IUPAC system[11,12] as $A_N + D_N$). The substitution can also proceed by a mechanism in which the first step involves elimination of the nucleofuge to give a nitrilium ion (pathway B), which then undergoes addition of the nucleophile to form product ($D_N + A_N$). The rate-limiting step in each of these mechanisms can be either the first or second step and examples of all four possibilities have been proposed[1–10] ($A_{N\#} + D_N$; $A_N + D_{N\#}$; $D_{N\#} + A_N$; and $D_N + A_{N\#}$).

A concerted mechanism (A_ND_N), pathway C in Scheme 1, cannot be unequivocally ruled out in certain substitution reactions at the carbon–nitrogen double bond.[1–3,8,9] There is, however, no compelling evidence for an A_ND_N mechanism in any nucleophilic substitution reaction at the carbon–nitrogen double bond studied so far, and the concerted pathway seems less likely than an addition–elimination mechanism or nitrilium ion formation. In vinylic systems, the possibility of bimolecular single-step nucleophilic substitutions has been discussed,[13–15] but it appears that most of the experimental and theoretical results point to an addition–elimination mechanism. On the other hand, there is considerable evidence that concerted nucleophilic substitutions do take place in certain acyl substrates.[16–24]

Ta-Shma and Rappoport[8,9] found what imidoyl chlorides [ArC(Cl)=NAr′] could react by the $D_N + A_N$ or the $A_N + D_N$ pathway depending on the nature of the substituents and the solvent for the reaction. In benzene solution[9] with electron-donating substituents, imidoyl chlorides reacted by the $D_N + A_N$ mechanism, albeit through ion pairs. In these reactions it was proposed that the nucleophilic attack on the ion pair was rate-limiting ($D_{Nint} + A_{N\#}$). When imidoyl chlorides substituted with electron-withdrawing groups were reacted with secondary amines, the substitution reactions proceeded by the $A_N + D_N$ pathway with rate-limiting addition. In acetonitrile solution,[8] imidoyl chlorides reacted by rate-determining ionization to nitrilium ions ($D_N + A_N$) regardless of the nature of substituents.

Similarly, benzohydrazonyl chlorides [ArC(Cl)=NNHAr′] react by the ionization mechanism in polar solvents and in the absence of good nucleophiles.[5] In solvents of low ionizing power with good nucleophiles, these reactions proceed by the $A_N + D_N$ mechanism with rate limiting addition.[6,7]

Ta-Shma and Rappoport[10] also investigated nucleophilic substitution on imidoyl cyanides

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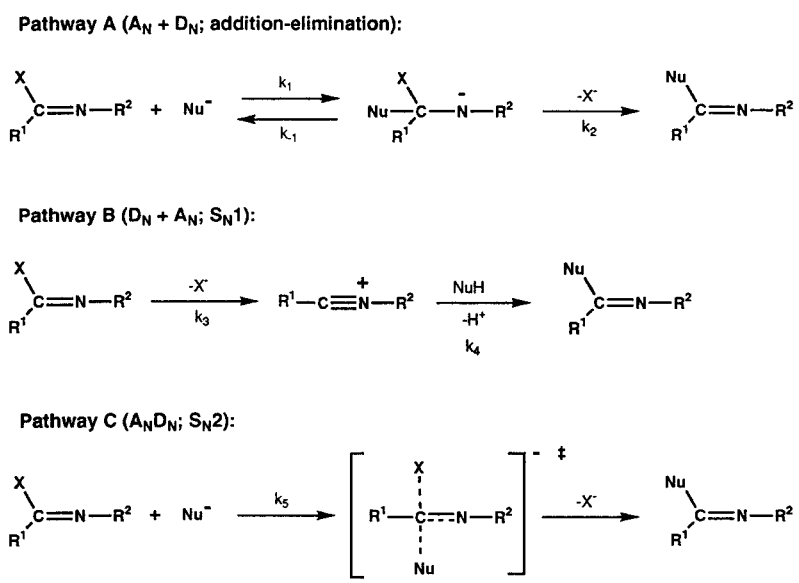


Scheme 1

[ArC(CN)=NAr'] with amines and alkoxides. Since cyanide ion is a much poorer nucleofuge than chloride ion, it was suggested that these substitution reactions proceed by an addition–elimination mechanism with elimination being the rate-limiting step ($A_N + D_{N\#}$).

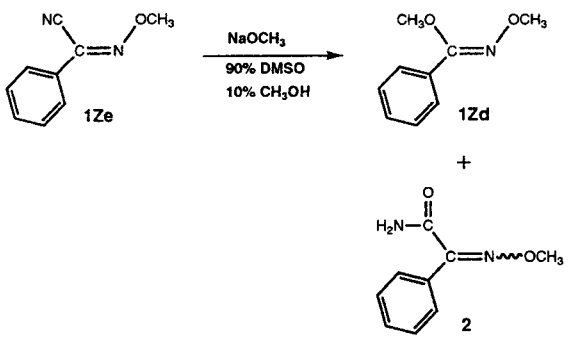
We have been investigating the kinetics and mechanisms of nucleophilic substitution reactions of hydroximoyl chlorides (**1Za**, **1Zb**, **1Ea** and **1Eb**, *N*-methoxyimidoyl chlorides) which undergo ionization to nitrilium ions ($D_N + A_N$) only under forcing conditions[4] (120 °C for **1Za** and 160 °C for **1Ea** in dioxane–water solutions). The hydroximoyl chlorides **1Za** and **1Ea** and their nucleophilic substitution products are resistant to thermal *E*–*Z* isomerization. Thus it has also been possible to investigate the stereochemistry of nucleophilic substitution. We have found that hydroximoyl chlorides react with methoxide ion,[3] pyrrolidine,[2] azetidine[1] and pyrrolidide ion[2] by addition–elimination mechanisms. It has been suggested that the addition step is rate determining in the case of reactions with methoxide and pyrrolidide ions, and the elimination step is rate determining in the reactions with pyrrolidine and azetidine.

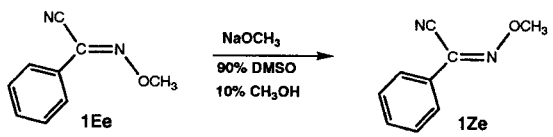
1Za and 1Ea: X = Cl; R = CH_3; Y = H
b: X = Cl; R = CH_3; Y = NO_2
c: X = OC_2H_5; R = CH_3; Y = H
d: X = OCH_3; R = CH_3; Y = H
e: X = CN; R = CH_3; Y = H
f: X = CN; R = CH_2CH_3; Y = H

RESULTS AND DISCUSSION

This report concerns the reactions of (*Z*)- and (*E*)-*O*-methylbenzohydroximoyl cyanides (**1Ze** and **1Ee**) with methoxide ion. We have previously reported the synthesis and identification of the (*Z*)- and (*E*)-hydroximoyl cyanides.[25,26] The methoxide substitution reactions were studied in 90% DMSO–10% methanol at 44·0 °C so the kinetic results could be compared directly with those obtained previously[3] on the reactions of methoxide ion with (*Z*)- and (*E*)-benzohydoximoyl chlorides (**1Za** and **1Ea**) and the *Z*- and *E*-isomers of ethyl *O*-methylbenzohydroximate (**1Zc** and **1Ec**).

The reaction of (*Z*)-*O*-methylbenzohydroximoyl cyanide (**1Ze**) with methoxide ion gave a mixture of two products, as shown. One of these products was methyl (*Z*)-*O*-methylbenzohydroximate (**1Zd**), which resulted from methoxide ion attack at the carbon–nitrogen double bond of **1Ze**. The other product, the *O*-methyloxime of α-ketophenylacetamide (**2**), resulted from nucleophilic attack on the cyano group of **1Ze**. It is assumed that an imidate is formed from nucleophilic attack on the cyano group. Hydrolysis of an imidate to





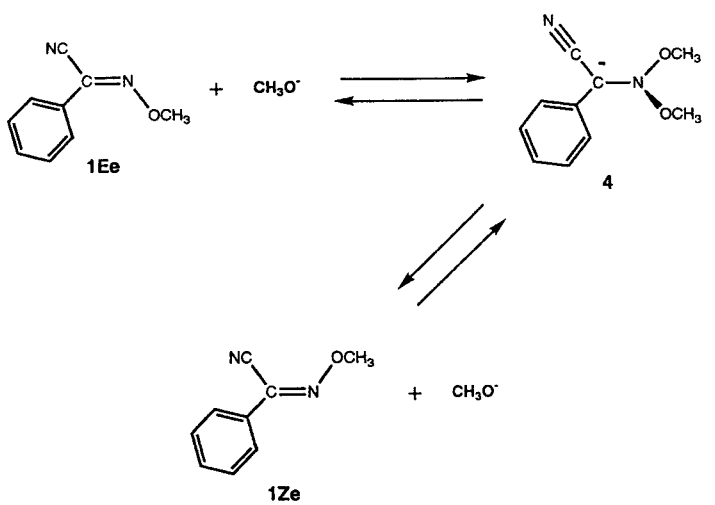
2 would be expected in working up the reaction or in HPLC analysis of the reaction mixture.

The reaction products **1Zd** and **2** are formed in about equal amounts. The kinetics of formation (Table 1) of these two products were measured at 44·8 °C under pseudo-first-order conditions using an HPLC method. The second-order rate constants decreased slightly with decrease in concentration of methoxide ion. The rate constant for methoxide ion substitution at the carbon–nitrogen double bond in **1Ze** is about 35 times smaller than that for nucleophilic substitution in the corresponding hydroximoyl chloride ($k_{1Za} = 1{\cdot}24 \times 10^{-2}$ l mol^{-1} s^{-1}).[3] When the methoxide ion substitution reaction of **1Ze** was followed to near completion, isomerization of the (*Z*)-hydroximate (**1Zd**) substitution product to the *E*-isomer was observed. We have measured the rate of this isomerization previously[3] and found that the second-order rate constant for the process is $1{\cdot}59 \times 10^{-5}$ l mol^{-1} s^{-1}, which is about 22 times smaller than the rate constant for methoxide ion substitution in the hydroximoyl cyanide **1Ze**.

Table 1. Second-order rate constants for the formation of **1Zd** and **2** from the reaction of (*Z*)-*O*-methylbenzohydroximoyl cyanide with sodium methoxide in dimethyl sulfoxide–methanol (9 : 1) at 44·6 °C

	10^4k (l mol^{-1} s^{-1})	
[MeO$^-$] (M)	**1Zd**	**2**
0·170	5·53	7·54
0·0588	4·34	6·65
0·0120	4·20	5·24
0·00612	3·50	3·56

When the (*E*)-hydroximoyl cyanide **1Ea** was reacted with methoxide ion, it underwent isomerization to the *Z*-isomer **1Za** faster than it underwent nucleophilic substitution. It is possible that this isomerization proceeds by nucleophilic attack at the nitrogen atom (azophilic attack, Scheme 2) of the carbon–nitrogen double bond to give a carbanion intermediate (**4**) rather than nucleophilic attack at carbon (carbophilic attack) to give a nitrogen anion. The carbanion produced by azophilic attack is a viable possibility since the carba-

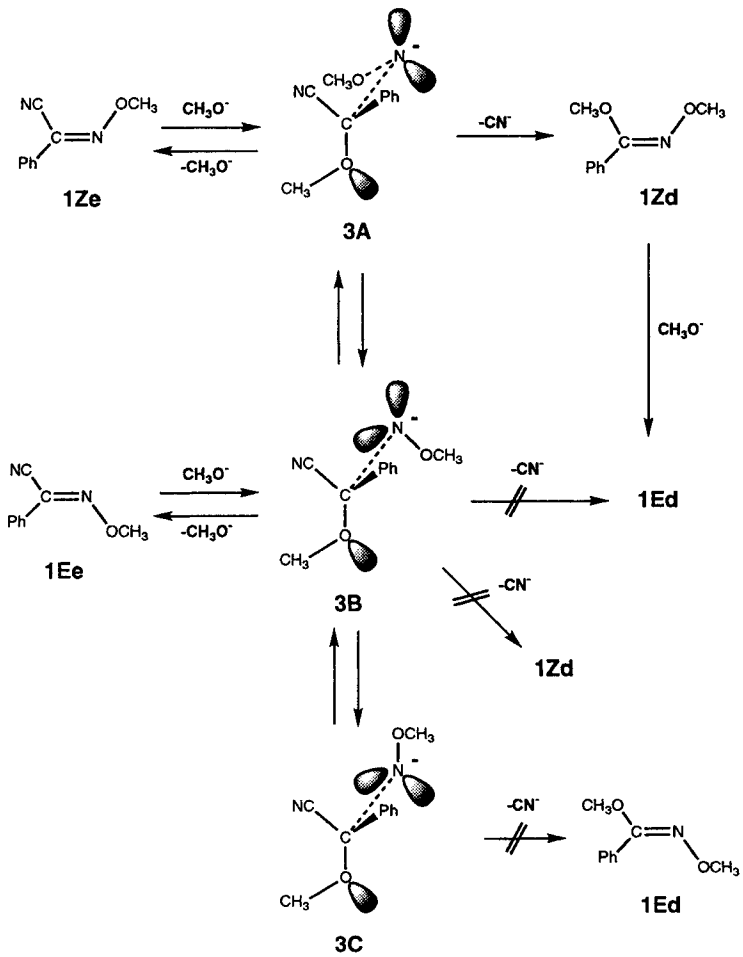


Scheme 2

nion produced from such an attack would be stabilized by both the cyano and phenyl groups. There are a few examples[27-29] of azophilic attack on the carbon–nitrogen double bond, although in all of these examples organometallic reagents were used as nucleophiles. In order to determine the mechanism of isomerization, (*E*)-*O*-ethylbenzohydroximoyl cyanide (**1Ef**) was isomerized to the *Z*-isomer in sodium methoxide solution. If the isomerization proceeds by azophilic attack it would be expected that there would be some exchange of the ethoxy group on nitrogen by methoxide ion. The isomerization of **1Ef** to **1Zf** in sodium methoxide solution was followed by HPLC and there was no evidence

Table 2. Second-order rate constants for the *Z*- to *E*-isomerization of *O*-alkylbenzohydroximoyl cyanides with sodium methoxide in dimethyl sulfoxide–methanol (9:1) at 44·6 °C

Compound	10^2[MeO$^-$] (M)	10^3k (l mol^{-1} s^{-1})
1Ee	0·830	9·47
1Ee	0·769	8·24
1Ee	2·03	8·28
1Ef	0·740	1·61
1Ef	0·940	2·78
1Ef	1·12	2·69
1Ef	1·25	2·35



k (E-cyanide ⟶ Z-cyanide) = 8.66 x 10^{-3}M^{-1}s^{-1}

k (hydroximate formation) = 3.50 x 10^{-4}M^{-1}s^{-1}

k (Z-hydroximate ⟶ E-hydroximate) = 1.59 x 10^{-5}M^{-1}s^{-1}

Scheme 3

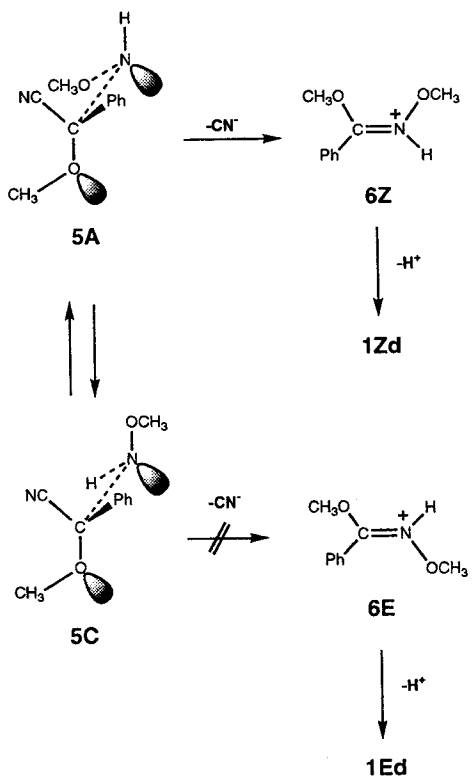
of alkoxy exchange during the isomerization, i.e. no **1Ze** or **1Ee** was formed during the isomerization of **1Ef** to **1Zf** in sodium methoxide solution.

The second-order rate constants for *E*- to *Z*-isomerization of **1Ee** and **1Ef** are given in Table 2. The second order *E*- to *Z*-isomerization rate constant for **1Ee** is about ten times greater than the rate constant for methoxide ion substitution at the carbon–nitrogen double bond in the *Z*-isomer (**1Ze**).

In this work, it was found that the (*E*)-hydroximoyl cyanide isomerizes to the *Z*-isomer under reaction conditions that eventually lead to substitution in the *Z*-isomer. This observation is consistent with an addition–elimination mechanism (Scheme 3) for the substitution in which the elimination of cyanide ion is rate determining ($A_N + D_{N\#}$). Rate-determining elimination of cyanide ion allows the tetrahedral intermediate to undergo stereomutation, which, in the case of the reaction of methoxide ion with the (*E*)-hydroximoyl cyanide, results in isomerization to the thermodynamically more stable *Z*-isomer.

It seems reasonable to assume that all the conformations of the tetrahedral intermediate (**3A**, **3B** and **3C** in Scheme 3) should be accessible during the reaction of the (*Z*)-hydroximoyl cyanide with methoxide ion. If this is the case, the *Z*/*E* product distribution should depend only on the relative energies of the transition states leading to the *Z*- and *E*-isomers (Curtin–Hammett principle[30]). There are two staggered transition states (*anti*-elimination from conformations **3A** and **3C**) and two eclipsed transition states (*syn*-elimination) that would have the incipient p-orbitals aligned properly in the transition state to form a π-bond. The eclipsed transition states should have a higher potential energy than those transition states derived from staggered conformations. Thus elimination should take place from conformations **3A** and **3C**. Reaction from conformation **3B** would not be as likely, since in the transition state for elimination the p-orbitals would not be aligned properly for π-bond formation.

In previous work, it was found that nucleophilic substitution on (*E*)-*O*-methylbenzohydroximoyl chloride (**1Ea**) either gives a mixture of *E*- and *Z*-substitution products (methoxide ion[3]) or predominately the *E*-substitution product (azetidine[1]). In these reactions it was suggested that the lifetime of the tetrahedral intermediate was so short that conformational



Scheme 4

equilibration of the intermediates did not take place. It was suggested that elimination of the nucleofuge took place from a transition state derived from a conformation analogous to **3B** to give an ylide intermediate.[1,3] In the case of the reaction of methoxide ion with the hydroximoyl cyanide **1Ee**, elimination of the poor nucleofuge from **3B** to form an ylid seems unlikely.

It is not clear why elimination of cyanide ion from **3A** would be preferred over elimination from **3C**. Since the initially formed substitution product **1Zd** is less thermodynamically stable than the *E*-isomer, one cannot attribute the preference for elimination from **3A** over **3C** to differences in stability of the incipient double bonds in the transition states for the formation of **1Zd** and **1Ed**. In the past, we have used stereoelectronic effects to rationalize our observations.[1-3] In this case there is no difference between **3A** and **3C** in this regard; both **3A** and **3C** have two unbounded electron pairs antiperiplanar to the nucleofuge.

It is possible that the elimination of cyanide ion could take place from the protonated tetrahedral intermediate (**5A** and **5C** in Scheme 4). The anion **3** should be strongly basic, so it seems likely the neutral tetrahedral intermediate would be present in this reaction. Elimination of cyanide ion from **5A** and **5C**, without assistance from methoxide ion, would give the protonated hydroximates **6Z** and **6E**. It is possible that the protonated (*Z*)-hydroximate (**6Z**) is more stable than the protonated *E*-isomer (**6E**), and as a result the energy of the transition state for formation of **6Z** would be lower than that for the transition state for formation of **6E**. At this time, we do not have experimental data either to support or to refute this hypothesis.

EXPERIMENTAL

General methods. DMSO was obtained from Burdick and Jackson (distilled in glass) and was stored over 4A molecular sieves. Methanol was also purchased from Burdick and Jackson. The hydroximoyl cyanides **1Ze** and **1Ee** were prepared according to published procedures.[25]

Melting points were measured on 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 45–65-mesh Chromosorb W.

HPLC analyses were carried out on an apparatus made up of a Spectra-Physics IsoChrome pump, an ISCO μLC-10 variable-wavelength UV–visible detector (set at 265 nm) fitted with a 10 mm pathlength cell, a Rheodyne injector and a Spectra-Physics SP4270 integrator.

Elemental analyses were performed at Atlantic Microlab (Norcross, GA, U.S.A.).

^{1}H NMR spectra were determined on a Varian EM-390 spectrometer and infrared spectra were determined with a Pye Unicam SP-1100 or a Midac Fourier transform IR spectrophotometer. Low-resolution mass spectra were obtained on a Varian Saturn 3 ion-trap GC–mass spectrometer.

Kinetic methods. The general procedure for preparation and thermostating the DMSO–methanol solutions has been described previously.[3] The reaction solutions were analyzed at appropriate time intervals by removing 5 ml aliquots from a 50 ml DMSO–methanol (9:1) solution (10^{-3}–10^{-4} M in hydroximoyl cyanide and 0·170–0·00612 M in sodium methoxide) that was thermostated at 44·6 °C (±0·1 °C). Water (10 ml) was added to each aliquot and 20 μl of each solution were injected into either a 25 × 0·46 cm i.d. Burdick and Jackson OC5 SG Octyl column (isomerization of **1Ee** and **1Ef** to **1Ze** and **1Zf**; mobile phase 55:45 acetonitrile–water) or a 25 × 0·46 cm i.d. Whatman Partisil 5 ODS-3 column (methoxide ion substitution on **1Ze**; mobile phase 55:45 acetonitrile–water). Both columns were protected from the strongly basic injection solution by guard columns which were replaced frequently. Normalization factors for peak areas were determined by analysis of samples containing known amounts of reactants and products.

Substitution product analysis. An 0·80 M solution of sodium methoxide in methanol (5·0 ml) was added to a solution of (*Z*)-*O*-methylbenzohydroximoyl cyanide (**1Ze**, 4·0 mmol) in DMSO (90 ml) and methanol (5 ml) and the reaction was suspended in a constant-temperature bath at 44·6 °C. After 48 h the reaction solution was poured into ice–water (100 ml). Sodium chloride was added to the aqueous solution until it was saturated, and the solution was extracted with ether (4 × 10 ml). The ether extracts were dried over anhydrous magnesium sulphate, and the ether was evaporated at aspirator pressure to give an oily residue. HPLC analysis of this oil showed that it contained only **2** and **1Zd**. The oil residues from several runs were combined and, after standing at room temperature for several weeks, a small amount of solid crystallized from the oil. The crystals were separated from the oil by vacuum filtration and washed with hexane. Recrystallization of the crystals from methanol–water gave the analytical sample of **2**, m.p. 142–145 °C; ^{1}H NMR ($CDCl_3$) δ 7·30–7·58 (m, 3H), 7·68–7·90 (m, 2H), 5·9–6·6 (2H), 4·09 (s, 3H); IR (KBr), 3490, 3340, 3190, 1700, 1610 cm^{-1}; MS, *m/z* (relative intensity, %) 178 (45, M^+), 134 (30), 119 (50), 104 (56), 103 (57), 77 (36), 76 (36), 51 (42), 49 (61), 44 (100); analysis, calculated for $C_9H_{10}N_2O_2$, C 60·67, H 5·.66, N 15·72; found, C 60·55, H 5·70, N 15·66%.

The filtrate was distilled in a short-path distillation apparatus (Kontes No. 284500) and the distillate was identified as methyl (*Z*)-*O*-methylbenzohydroximate

(**1Zd**) by comparison of its ^{1}H NMR and IR spectra with the spectra obtained from an authentic sample of **1Zd**.

(Z)-O-Ethylbenzohydroximoyl cyanide (**1Zf**). Using a procedure described previously (method B in Ref. 25), **1Zf** was obtained as a colourless oil after preparative GLC: ^{1}H NMR ($CDCl_3$), δ 7·65–8·20 (m, 2H), 7·25–7·65 (m, 3H), 4·44 (q, 2H, $J = 6$ Hz), 1·40 (t, 3H, $J = 6$ Hz); IR (neat), 1497 (w), 2230 cm^{-1}; MS, *m/z* (relative intensity, %), 174 (99, M^+), 146 (19), 116 (100), 89 (70), 77 (31), 51 (38); analysis, calcualted for $C_{10}H_{10}N_2O$, C 68·95, H 5·79, N 16·08; found, C 69·10, H 5·73, N 16·13%

(E)-O-Ethylbenzohydroximoyl cyanide (**1Ef**). Irradiation (254 nm) of a benzene solution of **1ZEf** gave a mixture of **1Ef** and **1Zf**. Preparative GLC of the mixture gave **1Ef** as a colourless oil: ^{1}H NMR ($CDCl_3$), δ 7·65–8·20 (m, 2H), 7·25–7·65 (m, 3H), 4·44 (q, 2H, $J = 6$ Hz), 1·38 (t, 3H, $J = 6$ Hz); IR (neat), 1551, 2232 cm^{-1}; analysis, calculated for $C_{10}H_{10}N_2O$, C 68·95, H 5·79, N 16·08; found, C 69·06, H 5·81, N 15·97%.

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