Laboratory-Scale Synthesis of Nitriles by Catalysed Dehydration of Amides and Oximes under Flash Vacuum Pyrolysis (FVP) Conditions

Jacqueline A. Campbell,[a] Graham McDougald,[b] Hamish McNab,*[b] Lovat V. C. Rees,†[b] Richard G. Tyas[b]

[a] Syngenta Crop Protection AG, Schwardzwaldallee 215, P.O. Box, 4002 Basel, Switzerland
Fax +41(61)3238971; E-mail: jacqui.campbell@syngenta.com

[b] School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK
Fax +44(131)6504743; E-mail: H.McNab@ed.ac.uk

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Dedicated to the memory of the late Professor Lovat Rees FRSE

Abstract: Dehydration of amides and oximes can be catalysed by 3 Å molecular sieves or by tungsten trioxide under flash vacuum pyrolysis (FVP) conditions. This provides a convenient synthesis of aliphatic, aromatic, and heterocyclic nitriles, generally in excellent yields under mild, neutral, and short contact time conditions.

Key words: gas-phase reaction, amides, oximes, nitriles, heterogeneous catalysis

Synthesis of nitriles by dehydration of amides or oximes is well established.[1] However, most reagents employed for these transformations suffer from practical disadvantages (e.g., toxicity, awkward reaction conditions, or work-up methods), and new methods continue to be reported.[2] It has been known since the dawn of organic chemistry that amides and oximes[3] can be dehydrated to nitriles under purely thermal conditions but the temperatures are too severe for all but the most stable of products.

As part of a program to develop green, solvent-free, reagent-free functional group transformations,[4] we have used these reactions as models to explore the effect of solid 'catalysts' under the short contact time conditions of a flash vacuum pyrolysis (FVP) experiment. Although the use of solid reagents under low-pressure flow conditions is well documented [e.g., the vacuum gas–solid reaction (VGSR) approach[5]], only isolated examples of catalysed reactions – including dehydrations – under short contact time conditions have been reported. Examples of alcohol dehydrations include generation and cyclisation of azaxylylene intermediates,[6] synthesis of 2-ethynylbutadiene[7] and formation of substituted siloles and germoles.[8] Catalysed stilbene oxide dehydration has also been reported.[9]

We report here the application of two general classes of furnace packing materials as dehydration catalysts under FVP conditions. First, 3A molecular sieve beads were specifically chosen as an example of a zeolite catalyst because the pore size is too small to accommodate organic molecules[10] so potential 'coking' problems are minimised. Tungsten trioxide powder was selected as an example of a metal oxide dehydration catalyst.[11] In both cases, a 10-gram plug of the catalyst was secured by silica wool in the centre of the furnace tube (2.5 cm diameter). The only pre-preparation of the catalysts was dehydration by heating in the FVP furnace prior to the pyrolysis.

First, a control experiment established the conditions required to effect dehydration of benzamide in our apparatus in the absence of catalyst, using porcelain saddles as an 'inert' furnace packing. Acceptable conversions were obtained only at temperatures above 800 °C, but these were associated with low recoveries of products. On the other hand, conversions of 95% were obtained when 3A molecular sieve pellets were used at temperatures above 400 °C – that is, at temperatures some 300–400 °C lower than in the absence of the catalyst (Figure 1). When tungsten trioxide was used as catalyst, the furnace temperature required was even lower (300–400 °C).

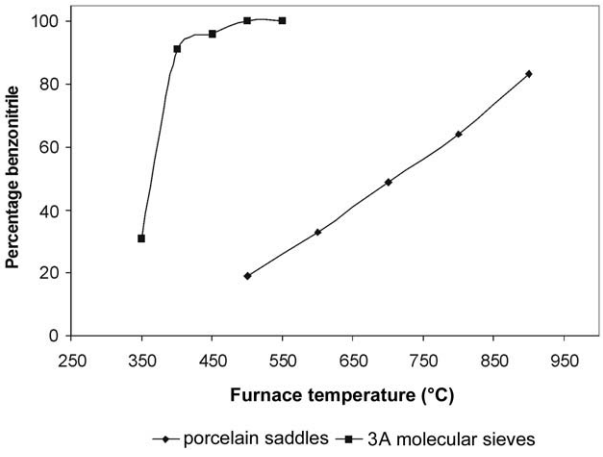

Figure 1 Temperature-conversion plot for the formation of benzonitrile from benzamide by FVP over porcelain saddles and 3A MS

Using the molecular sieve conditions, benzamide dehydration could be carried out with up to ca. 5 g of substrate, but on a larger scale, an increasing amount of starting material was recovered. This 'catalyst' deactivation is associated with the presence of the water formed during the reaction[12] and thermal reactivation proved impossible. Tungsten trioxide, on the other hand, could be used to dehydrate benzamide at 400 °C on a multigram scale without loss of activity and could be reactivated almost

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indefinitely. In both cases, throughput rate is likely to be a more important parameter than in the standard FVP experiment.[13] However, if incomplete conversion is obtained the reaction may be completed by repyrolysis of the mixture over fresh (or reactivated) catalysts.

The molecular sieve procedure was applicable, with minimal modification, to a wide range of aromatic, heteroaromatic and aliphatic amides **1** on a 0.5–1.0 gram scale (Table 1). Work-up methods were designed to remove unreacted starting material (if present – see experimental section) but often no other products were obtained. Representative examples in the aromatic series include the formation of *o*-toluonitrile (72%), and the *o*-, *m*- and *p*-aminobenzonitriles (75–99% yield) (Table 1, entries 2–5). Dehydration of a representative diamide provided the dinitrile (90%) under the standard conditions (Table 1, entry 7). Only the preparation of salicylonitrile was relatively unsatisfactory under these conditions (63%), requiring chromatographic separation; a small amount of cyanocyclopentadiene dimer (3%) was also identified from this reaction (Table 1, entry 6). Dehydration of both π-deficient and -excessive heterocyclic amides (Table 1, entry 8, and entries 9,10, respectively) took place in high yield under the standard conditions; the formation of the potentially sensitive furancarbonitrile[14] (95% yield) is particularly noteworthy (Table 1, entry 10). The relatively low yields of the aliphatic nitriles (Table 1, entries 11–14) may be due in part to work-up problems caused by their volatility. However, in each case, no other products were detected.

The tungsten trioxide method was also generally applicable (Table 1, entries 1,3,6,13, and 15). Some optimisation of furnace temperature was needed to maintain the quality of product but the procedure was easier to scale up than the molecular sieve method and the catalyst could be thermally reactivated and reused – or used for a different example – without compromising the yield or quality of product.

Dehydration of oximes **3** using 3A molecular sieves takes place under much milder FVP conditions (350 °C), than that of amides (see experimental section). Yields were generally high and no by-products were detected (Table 2). In particular, salicylonitrile was available in 87–88% yield by this procedure (Table 2, entry 2) without the problems associated with the corresponding amide pyrolysis. π-Excessive heterocyclic nitriles were prepared equally efficiently (see experimental section) (Table 2, entries 3–5). These systems are likely to be sensitive to many of the traditional reagents used for oxime dehydration. As with amide dehydration, the sieves were deactivated irreversibly during the procedure.

Dehydration of benzaldoxime worked well when catalysed by tungsten trioxide, even at the abnormally low temperature (for FVP) of 200 °C (Table 2). Other examples required higher furnace temperatures and although the yields were high, there was some discoloration of the product. In general, the molecular sieve method is preferred for oxime dehydrations on a small scale, provided deactivation of the catalyst is not a serious issue.

In conclusion, our catalysed gas-phase methods have provided robust, laboratory-scale procedures for the dehydration of aromatic, aliphatic and heterocyclic amides and oximes to the corresponding nitriles. No acidic reagents are used and there are none of the toxicity or work-up problems associated with most solution-phase methods

Table 1 Formation of Nitriles **2** by Catalytic Dehydration of Amides **1** under FVP Conditions

Entry	Precursor **1**, R	Yield (%) of **2** (3A MS, 500 °C)	Yield (%) of **2** (WO_3)
1	Ph	91	97 (400 °C)
2	*o*-MeC_6H_4	72	–
3	*o*-$H_2NC_6H_4$	99	87 (350 °C)
4	*m*-$H_2NC_6H_4$	79	–
5	*p*-$H_2NC_6H_4$	75	–
6	*o*-HOC_6H_4	63[a]	85 (400 °C)
7	*m*-$(CONH_2)C_6H_4$	90[b]	–
8	3-pyridyl	98	–
9	2-thienyl	82	–
10	2-furyl	95	–
11	Bn	60	–
12	*i*-Pr	59	–
13	*t*-Bu	65	87 (350 °C)
14	$Me(CH_2)_7$	73	–
15	$Me(CH_2)_4$	–	88 (300 °C)

[a] Chromatography required.
[b] Product is isophthalonitrile.

Table 2 Formation of Nitriles **2** by Catalytic Dehydration of Oximes **3** under FVP Conditions

Entry	Precursor **1**, R	Yield (%) of **2** (3A MS, 350 °C)	Yield (%) (WO_3)
1	Ph	97	92 (200 °C)
2	*o*-HOC_6H_4	88	87 (400 °C)
3	2-pyrrolyl	63	90 (400 °C)
4	3-indolyl	89	–
5	3-thienyl	77	–

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for accomplishing these transformations. The two catalysts used here each have their own advantages and disadvantages. Molecular sieves are cheap, and reaction conditions require little optimisation, but they work best on a small scale. Tungsten trioxide is easier to use on a multi-gram scale and the catalyst can be readily reactivated, but some optimisation of reaction conditions may be required.

^{1}H NMR and ^{13}C NMR spectra were recorded at 250 (or 200) MHz and 63 (or 50) MHz, respectively, for solutions in $CDCl_3$ unless otherwise stated. Chemical shifts are given in ppm relative to TMS; coupling constants are quoted in Hz.

Flash Vacuum Pyrolysis Experiments

Packing and Conditioning of the Catalysts

(a) *Molecular sieve method*: 3A MS (1–2 mm beads, 10 g) were packed into the centre of the silica FVP furnace tube (35 × 2.5 cm) and held in place by quartz wool to provide a catalyst plug of 2–3 cm in length. Before each procedure, the tube containing the catalyst was activated by heating in air for 2 h at the reaction temperature (or at 450 °C if the reaction temperature was less than 450 °C). The FVP apparatus was then assembled[13] and the catalyst was heated for a further 30 min at reaction temperature under vacuum.

(b) *Tungsten trioxide method*: WO_3 (>99%, powder, 10 g) was packed into the centre of the furnace tube (35 × 2.5 cm) and held in place by quartz wool to provide a catalyst plug of ca. 0.5 cm in length. It was heated at the reaction temperature in air for 30–60 min; the FVP apparatus was then assembled and the pyrolysis carried out.

Pyrolysis[13]

The substrate was distilled into the furnace tube and the products were trapped in a U-tube cooled by liquid nitrogen. Data are presented in the following order: quantity of substrate, inlet temperature, furnace temperature, pressure, time required for the pyrolysis and products.

Work-up

Method A: The pyrolysate was dissolved in MeOH and concentrated under reduced pressure. (Most amides and nitriles are soluble in MeOH so this method was used to provide information on the efficiency of the process, or if the product was insoluble in CH_2Cl_2.)

Method B: The nitrile component of the pyrolysate was dissolved in CH_2Cl_2, dried ($MgSO_4$), and the solvent was removed under reduced pressure. (This method was used to separate insoluble amide starting material.)

Method C: The pyrolysate was allowed to melt in the trap and the water droplet was cleanly removed with a pipette. The organic liquid was then removed from the trap and purified if necessary. (This method was used for liquid products.)

Optimisation of Amide Dehydration

Benzamide (ca. 1 mmol) was pyrolysed at temperatures ranging from 350 to 900 °C (Tables 3 and 4). The crude pyrolysate, in each case consisting of only benzamide and benzonitrile (identified by ^{13}C NMR spectroscopy), was worked up using Method A.

Dehydration of Amides; Typical Procedures

Benzonitrile

FVP of benzamide (461 mg, 3.8 mmol, 150 °C, 500 °C, 5×10^{-3} Torr, 20 min) over 3A MS gave, after work-up Method A, benzonitrile (359 mg, 91%).

^{1}H NMR (DMSO-d_6): δ = 7.74–7.43 (5 H, m).

Table 3 FVP of Benzamide (**1** R = Ph) over Porcelain Saddles (Inlet Temperature 150 °C)

Quantity (mg)	Furnace temp (°C)	Pressure (Torr)	Pyrolysis time (min)	Conversion (%)
148	500	0.005	5	19
163	600	0.005	5	33
167	700	0.005	5	49
180	800	0.005	5	64
162	900	0.005	5	83

Table 4 FVP of Benzamide (**1** R = Ph) over 3A MS (Inlet Temperature 150 °C)

Quantity (mg)	Furnace temp (°C)	Pressure (Torr)	Pyrolysis time (min)	Conversion (%)
150	350	0.005	15	31
366	400	0.005	15	91
429	450	0.005	20	96
461	500	0.005	20	100
572	550	0.005	20	100

^{13}C NMR (DMSO-d_6): δ = 133.25, 132.25 (2 CH), 129.47 (2 CH), 118.91 (C_q), 111.62 (C_q).

On a larger scale, FVP of benzamide (5.75 g, 56 mmol, 180 °C, 500 °C, 10^{-2} Torr, 120 min) over 3A MS gave benzonitrile (4.17 g, 85%) after work-up of the CH_2Cl_2-soluble fraction of the pyrolysate. The MeOH-soluble fraction yielded unreacted benzamide (0.67 g, 12%).

FVP of benzamide (4.98 g, 41 mmol, 180 °C, 400 °C, 2.3×10^{-2} Torr, 340 min) over WO_3 using work-up Method C gave only benzonitrile (4.11 g, 97%); data as above.

o-Tolunitrile

FVP of *o*-toluamide (555 mg, 4.1 mmol, 120 °C, 500 °C, 5×10^{-3} Torr, 25 min) over 3A MS using work-up Method B followed by distillation gave *o*-tolunitrile (348 mg, 72%); bp 95 °C/15 Torr (Lit.[15] bp 100–103 °C/15 Torr).

^{1}H NMR: δ = 7.62–7.09 (4 H, m), 2.46 (3 H, s).

^{13}C NMR: δ = 141.31 (C_q), 132.20, 131.92, 129.77, 125.78, 117.58 (C_q), 112.20, 19.88.

Anthranilonitrile

FVP of anthranilamide (910 mg, 6.7 mmol, 180 °C, 500 °C, 5×10^{-3} Torr, 40 min) over 3A MS using work-up Method B gave a colourless solid identified as anthranilonitrile (778 mg, 99%); mp 48–50 °C (Lit.[16] mp 50–51 °C).

^{1}H NMR: δ = 7.33–7.19 (2 H, m), 6.69–6.62 (2 H, m), 4.35 (2 H, br s).

^{13}C NMR: δ = 149.46 (C_q), 133.85, 132.20, 117.83, 117.47 (C_q), 115.00, 95.86 (C_q).

FVP of anthranilamide (971 mg, 7.1 mmol, 180 °C, 350 °C, 3.8×10^{-2} Torr, 80 min) over WO_3 using work-up Method A gave anthranilonitrile (732 mg, 87%); data as above.

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m-Aminobenzonitrile
FVP of *m*-aminobenzamide (824 mg, 6.1 mmol, 180 °C, 500 °C, 5 × 10^{-3} Torr, 30 min) over 3A MS using work-up method B yielded *m*-aminobenzonitrile (562 mg, 79%); bp 125 °C/0.2 Torr (Lit.[17] bp 160–163 °C/12 Torr).

^{1}H NMR: δ = 7.25–6.80 (4 H, m), 3.92 (2 H, br s).

^{13}C NMR: δ = 146.96 (C_q), 129.92, 121.71, 119.10 (2 signals, including 1 C_q), 117.27, 112.65 (C_q).

p-Aminobenzonitrile
FVP of *p*-aminobenzamide (855 mg, 6.3 mmol, 225 °C, 500 °C, 5 × 10^{-3} Torr, 35 min) over 3A MS using work-up Method B gave *p*-aminobenzonitrile (559 mg, 75%) as a colourless solid; mp 84–86 °C (Lit.[18] mp 84–86 °C).

^{1}H NMR: δ = 7.41–7.33 (2 H, m), 6.65–6.58 (2 H, m), 4.21 (2 H, br s).

^{13}C NMR: δ = 150.36 (C_q), 133.58 (2 CH), 120.07 (C_q), 114.21 (2 CH), 99.66 (C_q).

o-Cyanophenol
FVP of salicylamide (476 mg, 3.5 mmol, 180 °C, 500 °C, 5 × 10^{-3} Torr, 20 min) over 3A MS using work-up Method A gave a light brown solid mixture which was separated by dry-flash chromatography, providing *o*-cyanophenol (258 mg, 63%); mp 94–96 °C (Lit.[19] mp 97–98 °C).

^{1}H NMR (DMSO-d_6): δ = 11.05 (1 H, br s), 7.57–7.41 (2 H, m), 7.00–6.84 (2 H, m).

^{13}C NMR (DMSO-d_6): δ = 160.41 (C_q), 134.93, 133.44, 119.75, 117.26 (C_q), 116.37, 99.04 (C_q).

A minor component was unambiguously identified as the dimer(s) of 1-cyanocyclopentadiene (10 mg, 3%) by comparison of its NMR spectra with those of an authentic sample.[20]

FVP of salicylamide (1000 mg, 7.3 mmol, 145 °C, 400 °C, 2.5 × 10^{-2} Torr, 74 min) over WO_3 using work-up Method A gave *o*-cyanophenol as an off-white solid (825 mg, 95% material recovery, ca. 85% yield); mp 94–96 °C (Lit.[19] mp 97–98 °C); spectroscopic data as above.

A minor component was tentatively identified as phenol (8%) by comparison of its NMR spectra with those of an authentic sample.

Isophthalonitrile
FVP of isophthalamide (315 mg, 1.9 mmol, 280 °C, 500 °C, 3 × 10^{-3} Torr, 15 min) over 3A MS using work-up Method A gave isophthalonitrile (220 mg, 90%) as a white solid; mp 161–163 °C (Lit.[21] mp 163 °C).

^{1}H NMR: δ = 8.48 (1 H, m), 8.20 (2 H, m), 7.79 (1 H, m).

^{13}C NMR (DMSO-d_6): δ = 136.93 (2 CH), 136.22, 130.81, 117.30 (2 C_q), 112.87 (2 C_q).

Nicotinonitrile
FVP of nicotinamide (1.011 g, 8.3 mmol, 150 °C, 500 °C, 1 × 10^{-3} Torr, 40 min) over 3A MS using work-up Method A gave nicotinonitrile as a colourless solid (843 mg, 98%); bp 75 °C/10 Torr (Lit.[22] bp 98 °C/23 Torr).

^{1}H NMR: δ = 8.80–8.72 (2 H, m), 7.90 (1 H, m), 7.38 (1 H, m).

^{13}C NMR: δ = 152.73, 152.15, 139.01, 123.38, 116.23 (C_q), 109.78 (C_q).

Thiophene-2-carbonitrile
FVP of 2-thiophenecarboxamide (998 mg, 7.9 mmol, 180 °C, 500 °C, 5 × 10^{-3} Torr) over 3A MS using work-up Method A followed by distillation gave a clear oil identified as thiophene-2-carbonitrile (704 mg, 82%); bp 30 °C/0.6 Torr (Lit.[23] bp 57 °C/2.5 Torr).

^{1}H NMR: δ = 7.93 (1 H, m), 7.82 (1 H, m), 7.18 (1 H, m).

^{13}C NMR: δ = 138.42, 134.37, 128.05, 114.37 (C_q), 108.66 (C_q).

Furan-2-carbonitrile
FVP of 2-furancarboxamide (838 mg, 7.6 mmol, 90 °C, 500 °C, 5 × 10^{-3} Torr, 40 min) over 3A MS using work-up Method B provided furan-2-carbonitrile (666 mg, 95%).[24]

^{1}H NMR: δ = 7.57 (1 H, m), 7.09 (1 H, m), 6.52 (1 H, m).

^{13}C NMR: δ = 147.20, 126.10 (C_q), 121.84, 111.29, 111.25 (C_q).

Phenylacetonitrile
FVP of phenylacetamide (410 mg, 3.0 mmol, 225 °C, 500 °C, 5 × 10^{-3} Torr, 20 min) over 3A MS using work-up Method B followed by distillation gave phenylacetonitrile as a clear oil (214 mg, 60%); bp 80 °C/0.6 Torr (Lit.[23] bp 80 °C/0.5 Torr).

^{1}H NMR: δ = 7.36–7.18 (5 H, m), 3.67 (2 H, s).

^{13}C NMR: δ = 129.69 (C_q), 128.68 (2 CH), 127.57, 127.52 (2 CH), 117.64 (C_q), 23.03.

Isobutyronitrile
FVP of isobutyramide (225 mg, 2.6 mmol, 90 °C, 500 °C, 1 × 10^{-2} Torr, 15 min) over 3A MS using work-up Method B gave isobutyronitrile (140 mg, 59%).[25]

^{1}H NMR: δ = 2.69 (1 H, sept, *J* = 7.0 Hz), 1.31 (6 H, d, *J* = 7.0 Hz).

^{13}C NMR: δ = 123.61 (C_q), 19.76, 19.66.

Trimethylacetonitrile
FVP of trimethylacetamide (299 mg, 3.0 mmol, 90 °C, 500 °C, 1×10^{-2} Torr, 15 min) over 3A MS using work-up Method A gave trimethylacetonitrile (159 mg, 65%).[25]

^{1}H NMR: δ = 1.34 (9 H, s).

^{13}C NMR: δ = 125.70 (C_q), 28.18, 27.86 (C_q).

FVP of trimethylacetamide (1.014 g, 10.0 mmol, 115 °C, 350 °C, 2.6 × 10^{-2} Torr, 110 min) over WO_3 using work-up Method C gave trimethylacetonitrile as a colourless liquid (724 mg, 87%), spectroscopic data as above.

Pelargononitrile
FVP of pelargonamide (314 mg, 2.0 mmol, 90 °C, 500 °C, 5 × 10^{-3} Torr, 15 min) over 3A MS using work-up Method B gave pelargononitrile (203 mg, 73%); bp 65 °C/0.5 Torr (Lit.[26] bp 63–64 °C/0.5 Torr).

^{1}H NMR: δ = 2.29 (2 H, t, *J* = 7.0 Hz), 1.64–1.58 (2 H, m), 1.43–1.37 (2 H, m), 1.25–1.24 (8 H, m), 0.87–0.81 (3 H, m).

^{13}C NMR: δ = 119.57 (C_q), 31.41, 28.68, 28.44, 28.37, 25.10, 22.31, 16.80, 13.74.

Hexanonitrile
FVP of hexanamide (878 mg, 7.6 mmol, 120 °C, 300 °C, 2.6 × 10^{-2} Torr, 65 min) over WO_3 using work-up Method C gave hexanonitrile as a colourless liquid (648 mg, 88%); bp 162–164 °C/760 Torr (Lit.[27] bp 162–163 °C/760 Torr).

^{1}H NMR: δ = 2.32 (2 H, t, *J* = 7.0 Hz), 1.72–1.58 (2 H, m), 1.49–1.28 (4 H, m), 0.94–0.87 (3 H, m).

^{13}C NMR: δ = 119.70 (C_q), 30.55, 24.85, 21.66, 16.88, 13.54.

Optimisation of Oxime Dehydration
Benzaldehyde oxime (ca. 1 mmol) was pyrolysed over 3A MS at temperatures ranging from 300 to 450 °C as described above for amide dehydration. The crude pyrolysate, in each case consisting of

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only benzaldehyde oxime and benzonitrile, was collected into CH_2Cl_2, dried ($MgSO_4$) and concentrated under reduced pressure. The parameters are given in Table 5.

Table 5 FVP of Benzaldoxime (**3** R = Ph) over 3A MS (Inlet Temperature 60 °C)

Quantity (mg)	Furnace temp (°C)	Pressure (Torr)	Pyrolysis time (min)	Conversion
127	300	0.01	10	>90
97	350	0.01	10	>90
109	400	0.01	10	>90
80	450	0.01	10	100

Dehydration of Oximes; Typical Procedures

Benzonitrile

FVP of benzaldoxime (97 mg, 8.0 mmol, 60 °C, 350 °C, 1×10^{-2} Torr, 10 min) over 3A MS using work-up Method B gave benzonitrile (80 mg, 97%); spectroscopic data as above.

FVP of benzaldoxime (991 mg, 8.2 mmol, 95 °C, 200 °C, 7.0×10^{-2} Torr, 80 min) over WO_3 using work-up Method C gave benzonitrile as a clear liquid (781 mg, 92%); spectroscopic data as above.

2-Cyanophenol

FVP of salicylaldoxime (808 mg, 5.9 mmol, 180 °C, 350 °C, 5×10^{-3} Torr, 30 min) over 3A MS using work-up Method B provided a yellow solid which, after distillation, was identified as 2-cyanophenol (621 mg, 88%); mp 90–93 °C (Lit.[19] mp 97–98 °C); spectroscopic data as above.

FVP of salicylaldoxime (1001 mg, 7.3 mmol, 145 °C, 400 °C, 3.0×10^{-2} Torr, 36 min) over WO_3 using work-up Method A gave 2-cyanophenol as a dark yellow solid (758 mg, 87%); mp 93–95 °C (Lit.[19] mp 97–98 °C); spectroscopic data as above.

Pyrrole-2-carbonitrile

FVP of pyrrole-2-carbaldoxime (870 mg, 7.9 mmol, 150 °C, 350 °C, 1×10^{-3} Torr, 120 min) over 3A MS using work-up Method B gave pyrrole-2-carbonitrile (457 mg, 63%) as an orange oil; bp 80 °C/0.3 Torr (Lit.[28] bp 89–90 °C/1.5 Torr).

^{1}H NMR: δ = 9.65 (1 H, br s), 6.86 (1 H, dd, *J* = 2.7, 1.4 Hz), 6.79 (1 H, dd, *J* = 3.8, 1.4 Hz), 6.17 (1 H, dd, *J* = 3.8, 2.7 Hz).

^{13}C NMR: δ = 123.78, 120.11, 114.77 (C_q), 109.84 and 100.28 (C_q).

FVP of pyrrole-2-carbaldoxime (971 mg, 8.8 mmol, 170 °C, 400 °C, 2.5×10^{-2} Torr, 30 min) over WO_3 using work-up Method B gave pyrrole-2-carbonitrile as a dark yellow liquid (732 mg, 90%); bp 38–43 °C/0.05 Torr (Lit.[28] bp 89–90 °C/1.5 Torr); spectroscopic data as above.

Indole-3-carbonitrile

FVP of indole-3-carbaldoxime (613 mg, 3.8 mmol, 240 °C, 350 °C, 1×10^{-2} Torr, 25 min) over 3A MS using work-up Method A gave indole-3-carbonitrile (484 mg, 89%) as an orange solid; mp 177–181 °C (Lit.[29] mp 183–184 °C).

^{1}H NMR (DMSO-d_6): δ = 8.23 (1 H, s), 7.65–7.43 (2 H, m), 7.34–7.15 (2 H, m).

^{13}C NMR: δ = 135.35 (C_q), 134.60, 126.87 (C_q), 123.54, 121.85, 118.57, 116.57 (C_q), 113.09, 84.36 (C_q).

Thiophene-3-carbonitrile

FVP of thiophene-3-carbaldoxime (318 mg, 2.5 mmol, 135 °C, 350 °C, 1×10^{-2} Torr, 15 min) over 3A MS using work-up Method A yielded thiophene-3-carbonitrile after distillation as a clear oil (209 mg, 77%); bp 210 °C/760 Torr (Lit.[30] bp 203–205 °C/760 Torr).

^{1}H NMR: δ = 9.02 (1 H, dd, *J* = 3.0, 1.2 Hz), 7.40 (1 H, dd, *J* = 5.1, 3.0 Hz), 7.27 (1 H, dd, *J* = 5.1, 1.2 Hz).

^{13}C NMR: δ = 135.22, 128.43, 127.12, 114.90 (C_q), 110.37 (C_q).

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