Addition of nucleophiles to (*E*)-3-phenylsulfonylprop-2-enenitrile: a route to β-substituted α,β-unsaturated nitriles and to acetals of cyanoacetaldehyde

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Dedicated to Professor M. Anthony McKervey on his 65th birthday

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Abstract

(*E*)-3-Phenylsulfonylprop-2-enenitrile reacts with sulfur-, oxygen- and carbon-based nucleophiles to yield (*E*)-configured β-substituted α,β-unsaturated nitriles *via* a regiospecific addition-elimination sequence.

Keywords: Nitrile, unsaturated, heterosubstituted

Introduction

We have recently reported[1] on the powerful dienophilic reactivity of (*E*)-3-phenylsulfonylprop-2-enenitrile **1**. This strongly electron-deficient alkene undergoes facile cycloaddition reactions with a variety of dienes to yield Diels-Alder adducts. We demonstrated that benzenesulfinic acid could be eliminated from some of these adducts when they were treated with the strong base potassium *tert*-butoxide: compound **1** is therefore an effective cyanoacetylene **2** equivalent in cycloaddition chemistry. Cyanoacetylene itself is a relatively unstable[2] species, existing[3] in interstellar dust clouds and in the atmosphere of Titan, the largest moon of Saturn.

1 **2**

Figure 1

We considered that the nitrile **1** should also be capable of acting as a cyanoacetylene equivalent in nucleophilic addition reactions. Thus (Figure 2), reaction of **1** with a nucleophile at its sulfonyl-substituted olefinic carbon atom should lead to the trisubstituted addition product **3**. Subsequent base-catalysed elimination of benzenesulfinic acid from **3** should then yield a β-substituted α,β-unsaturated nitrile **4**. In an alternative reaction pathway, where **1** might act as an equivalent for phenylsulfonylethyne **5**, a nucleophile could attack **1** at C-2, leading to a different addition product **6**. Elimination of hydrogen cyanide from **6** would then give an α,β-unsaturated sulfone **7**.

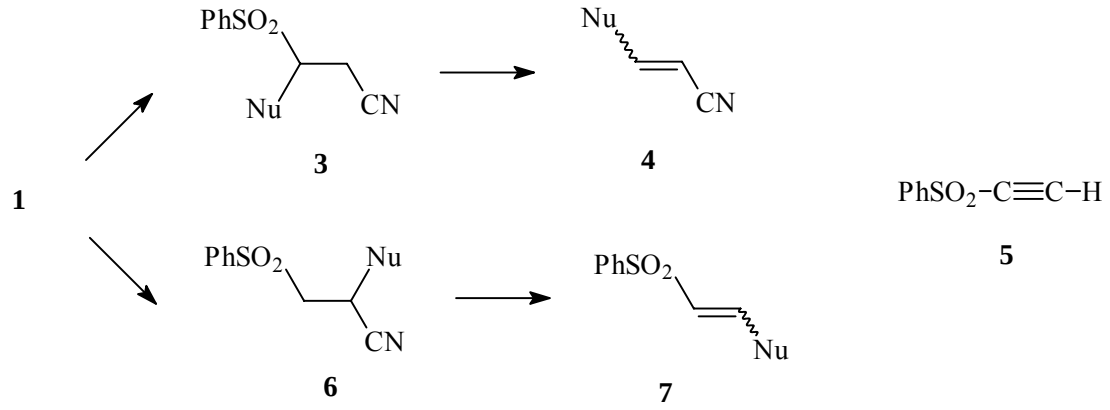


Figure 2

The regioselectivity of a reaction between a nucleophile and the alkene **1** is difficult to predict *ab initio*. Nesmeyanov *et al.*[4] have suggested that the regioselectivities of nucleophilic addition reactions to ethenes **8** bearing different electron-withdrawing groups at C-1 and at C-2 may be determined by the relative stabilities of the intermediate carbanionic species **9** and **10**. Although this approach fails to take account of factors such as solvation and steric hindrance it provides a useful starting point for considering these reactions.

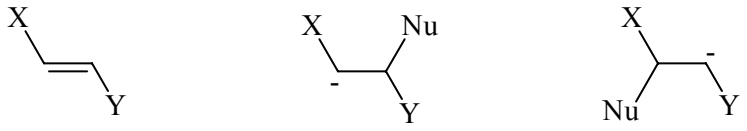


Figure 3

Reactions of the Michael acceptor **1** with the secondary amine pyrrolidine have been described by Benedetti *et al.*[5] When an excess of pyrrolidine was employed the major products obtained from these reactions were the β-amino-α,β-unsaturated nitrile **11** and the β-amino-α,β-

unsaturated sulfone **12**, formed in 1 : 1 ratio. Following Nesmayanov,[4] this result was interpreted as reflecting the comparable stabilities of each of the intermediate carbanions **13** and **14** (pK_a for H_3CSO_2Ph = 29; pK_a for H_3CCN = 31: both values are for DMSO solutions[6]).

The same group[5] also investigated the reaction of **1** with methanol in the presence of catalytic amounts of sodium methoxide. The acetal **15** was obtained as the sole product, presumably *via* further addition of methoxide ion to β-methoxyacrylonitrile **16** that was formed by an initial addition-elimination reaction between the sulfonylnitrile **1** and methoxide. Benedetti *et al*. suggest[5] that the regioselectivity of this overall reaction is only apparent, that both of the intermediate carbanions **17** and **18** are actually formed, and that the outcome reflects the fact that elimination of cyanide ion from **18** cannot compete with the elimination of the better leaving group methoxide.

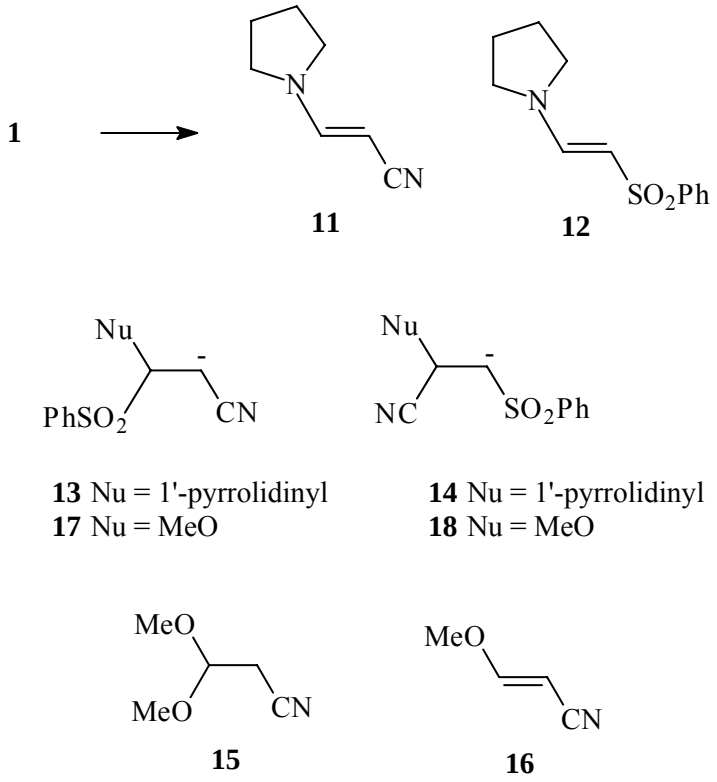


Figure 4

It was clear that a study of the reactions between the reactive alkene **1** and a wider spectrum of nucleophiles was warranted. In this paper we describe the outcome of our investigations into the addition reactions between **1** and a range of sulfur-, oxygen- and carbon-based species.

Results and Discussion

We first examined the reactions of the nitrile **1** with thiophenol. When exposed to one equivalent each of thiophenol and triethylamine in chloroform solution (*E*)-β-thiophenylacrylonitrile **19** was obtained in 76% yield. This compound has been synthesised previously by several authors,[7-9] but each of the routes that have been described are multi-step, and most give mixtures of (*E*)- and (*Z*)-products. We did not detect measurable amounts of (*Z*)-isomers in this or any of the other addition - elimination reaction products described in this paper.

When **1** was reacted with a fourfold excess of each of thiophenol and triethylamine the thioacetal **20** (90%) was formed. This compound represents a masked form of cyanoacetaldehyde, and has been synthesised previously *via* a less direct route.[10]

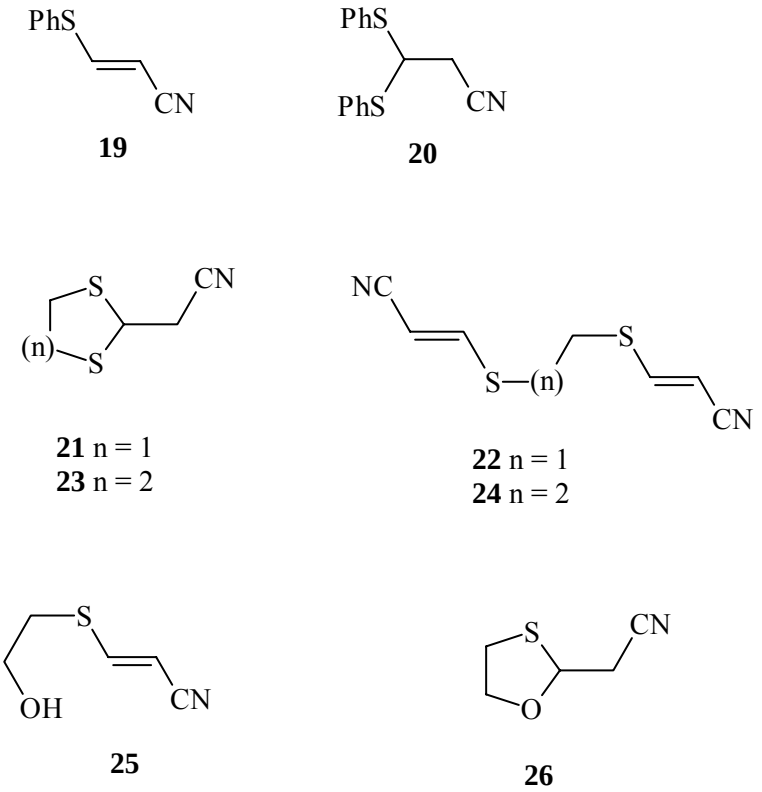


Figure 5

Reactions of (*E*)-phenylsulfonylprop-2-enenitrile **1** with dithiols could be controlled to yield either monomeric or dimeric products. Thus, when **1** was reacted with one equivalent of ethanedithiol in the presence of four equivalents of triethylamine the major product was 2-cyanomethyl-1,3-dithiolane **21** (77%).[11] The minor product of this reaction was the dimeric thioenol ether **22**. Similar results were obtained when propane-1,3-dithiol was employed as nucleophile, yielding 2-cyanomethyl-1,3-dithiane **23** (53%), together with lesser amounts of the

bis-thioether **24**. The dimeric products **22** and **24** could be made to predominate (in yields of, respectively, 89 and 94%) by reacting two equivalents of **1** with one equivalent of dithiol in the presence of triethylamine. The dithiane **23** has been previously obtained in 26% yield *via* reaction of the chlorozinc derivative of 1,3-dithiane with iodoacetonitrile.[12]

When 2-hydroxyethanethiol was used as the nucleophile, addition to **1** took place exclusively through its sulfur atom in the presence of triethylamine, to yield the thioenol ether **25** (47%). No trace of the oxathiolane **26**, a potential cyclisation product, could be detected.

Failure of the hydroxyl group of **25** to undergo an intramolecular nucleophilic addition reaction under the conditions that were employed was duplicated when we attempted to carry out the addition of alcohols to **1** under the same regime. However, reaction of **1** with a slight excess of sodium ethoxide in THF afforded β-ethoxyprop-2-enenitrile **27** in 51% yield. This contrasts with the result obtained by Benedetti *et al*.[5] who obtained the acetal **15**, the product of sequential addition-elimination-addition reactions, by reaction of **1** with catalytic sodium methoxide in methanol. We have obtained the corresponding diethyl acetal **28** in 72% yield by reaction of **1** with an excess of sodium ethoxide in THF. An advantage of using our conditions is that reaction can be terminated at the β-alkoxypropenenitrile stage. The syntheses of some β-alkoxypropenenitriles have been described by Scotti,[13] who prepared them from the (*E*)- or (*Z*)-isomers of 3-chloropropenenitrile, and also by Prange[14] who utilised a more complex route involving high-pressure condensation of the anion of acetonitrile with carbon monoxide, followed by trapping of the derived enolate using chloroethane.

27 R = Et
29 R = Ph
30 R = H_2C=CH(Me)CH_2
31 R = HC≡CCH_2

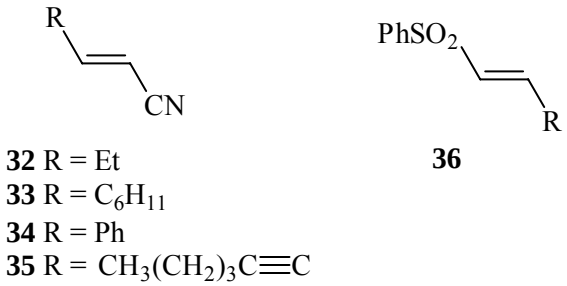
28

Figure 6

The sodium salt of phenol, and the sodium alkoxides derived from each of 2-methylprop-2-enol and prop-2-ynol were successfully reacted with (*E*)-phenylsulfonylprop-2-enenitrile **1** to give, respectively, the (*E*)-configured addition-elimination products **29** (60%), **30** (53%) and **31**. The propargyl ether **31** was obtained in 63% yield after purification: its (*Z*)-isomer has been synthesised[15] *via* addition of propargyl alcohol to cyanoacetylene in the presence of either K_2CO_3 (5% yield) or NaOMe (30% yield).

We next examined the addition of carbon nucleophiles to **1**. All attempts to effect the addition of stabilised carbanionic species, such as the anions of diethyl malonate, ethyl acetoacetate or pentane-2,4-dione, met with failure. The starting material **1** was recovered, and material derived from it *via* probable anionic polymerisation[1] was formed. However, the addition

of Grignard reagents to (*E*)-phenylsulfonylprop-2-enenitrile **1** proceeded smoothly at the sulfonyl terminus to give the expected products of an addition-elimination sequence. Thus, ethyl-, cyclohexyl-, phenyl- and hex-1-ynylmagnesium halides all afforded useful yields of the derived (*E*)-α,β-unsaturated nitriles **32** (57%), **33** (59%), **34** (78%) and **35** (68%). The α,β-unsaturated sulfones **36** that would result from **1** *via* attack of an organomagnesium compound at C-2 were not detected. Since the addition of an organomagnesium reagent to **1** cannot be a reversible process we conclude that nucleophilic attack by the organometallic takes place regiospecifically at C-3.



32 R = Et
33 R = C_6H_{11}
34 R = Ph
35 R = $CH_3(CH_2)_3C{\equiv}C$

36

Figure 7

Conclusions

In summary, (*E*)-3-benzenesulfonyl-prop-2-enenitrile **1** reacts regiospecifically with sulfur-, oxygen- and carbon-based nucleophiles to afford, initially, β-substituted-α,β-unsaturated nitriles. These then undergo β-elimination of benzenesulfinic acid to give (*E*)-configured α,β-unsaturated nitriles. Yields of these nitriles are generally good and, in some cases, are superior to those obtained by using alternative procedures.

Experimental Section

General Procedures. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ using a JEOL PMX-60 spectrometer. Coupling constants *J* are reported in Hz. IR spectra were recorded as liquid films (L) or Nujol mulls (N) using Perkin-Elmer 298, Perkin-Elmer 883 or Paragon FT-IR instruments. Melting points were obtained using a Stuart Scientific SMP2 apparatus and are uncorrected. TLC was performed using Merck $60F_{254}$ silica-coated plates. Column chromatography was carried out using Merck Kieselgel 60, 70-230 mesh. All solvents were distilled before use. Elemental analyses were performed by the Microanalytical Laboratory, University College Dublin.

(*E*)-3-Phenylsulfonylprop-2-enenitrile (1). Was prepared as described by us[1] and had m. p. 93-94 °C (ethyl acetate - hexane).

(*E*)-3-Thiophenylprop-2-enenitrile (19). The sulfone **1** (4.0 g, 20 mmol) and freshly distilled thiophenol (2.28 g, 20 mmol) were dissolved in chloroform (50 mL). To this stirred solution was added triethylamine (2.1 g, 20 mmol) at such a rate that the temperature of the mixture did not exceed 25 °C. After 2 hr the solvent was evaporated, the residue was taken up in ether and the ethereal extract was washed with hydrochloric acid solution and then with sodium hydroxide solution. The extract was dried, solvent was removed, and the residue was distilled to give the product **19** as an oil (2.53 g, 76%), b. p. 98-102 °C/0.2 mm Hg, [*lit*.[9] b. p. 95-103 °C/0.1 mm Hg], ν_{max} (L) 2220, 1565, 750 and 690 cm^{-1}, δ_H (60 MHz) 4.90 (1H, d, *J* 16, 2-H), 7.30 (1H, d, *J* 16, 3-H) and 7.30 (5H, m, ArH) ppm. Found: C 67.33, H 4.44, N 8.72%. Calculated for C_9H_7NS: C 67.05, H 4.38, N 8.69%

3,3-Di(thiophenyl)propanenitrile (20).

(a) From (E)-3-phenylsulfonylprop-2-enenitrile (1). To a stirred solution of the sulfone **1** (1.93 g) in chloroform (30 mL) with thiophenol (4.4 g, 4 eq.) was added triethylamine (4.04 g, 4 eq.) at such a rate that the temperature did not rise about 20 °C. After 2 hr solvent was evaporated at reduced pressure and the residue was taken up in ether. The extract was washed sequentially with dilute hydrochloric acid and with sodium hydroxide solution, dried and evaporated to yield the thioacetal **20** as an oil (2.44 g, 90%) (*lit*.[10] an oil), b. p. 165 °C/0.2 mm Hg, ν_{max} (L) 2225, 1575, 750 and 690 cm^{-1}, δ_H (60 MHz) 2.66 (2H, d, *J* 7, -C*H*$_2$CN), 4.38 (1H, t, *J* 7, -C*H*CH_2CN) and 7.1-7.5 (10H, m, Ar*H*) ppm. Found: C 66.19, H 4.58, N 5.10%. Calculated for $C_{15}H_{13}NS_2$: C 66.42, H 4.79, N 5.17%

(b) From (E)-3-Thiophenylprop-2-enenitrile (19). To a stirred solution of the nitrile **19** (1.61 g, 10 mmol) in chloroform (30 mL) with thiophenol (1.1 g, 10 mmol) was added triethylamine (1.01 g, 10 mmol). After 2 hr, work-up as described above afforded the thioacetal **20** (1.85 g, 68%).

2-Cyanomethyl-1,3-dithiolane (21). [11] To a stirred solution of the sulfone **1** (1.93 g, 10 mmol) in chloroform (30 mL) was added, in one portion, a mixture of 1,2-ethanedithiol (0.92 g, 10 mmol) and triethylamine (4.04 g, 4 eq.). After 2 hr the reaction mixture was diluted with chloroform and washed with aqueous hydrochloric acid and with aqueous sodium hydroxide solution. After drying, evaporation of solvent yielded the dithiolane **21** as an oil (1.12 g, 77%), b. p. 108 °C/0.2mm Hg, ν_{max} (L) 2230 and 1415 cm^{-1}, δ_H (60 MHz) 2.80 (2H, d, *J* 6, -C*H*$_2$CN), 3.30 (4H, s, -SC*H*$_2$C*H*$_2$S-) and 4.60 (1H, t, *J* 6, -C*H*-CH_2CN) ppm. Found: C 41.28, H 4.67, N 9.51%. Calculated for $C_5H_7NS_2$: C 41.38, H 4.83, N 9.65%.

(*E*,*E*)-4,7-Dithiadeca-2,8-diene-1,10-dinitrile (22). To a stirred solution of the sulfone **1** (1.93 g, 10 mmol) in chloroform (30 mL) was added 1,2-ethanedithiol (0.46 g, 5 mmol). Triethylamine (1.01 g, 1 eq.) was added dropwise during 0.5 hr. After a further 1.5 hr the reaction mixture was diluted with chloroform and washed with aqueous hydrochloric acid and with aqueous sodium hydroxide solution. After drying, evaporation of solvent followed by recrystallisation from hexane yielded the dithiadecadiene **22** as a solid (0.87 g, 89%), m. p. 116-

117 °C, ν_{max} (N) 2205, 1565, 950 and 855 cm^{-1}, δ_H (60 MHz) 3.26 (4H, s, -SC*H*$_2$C*H*$_2$S-), 5.46 (2H, d, *J* 16, -CH=C*H*CN) and 7.46 (2H, d, *J* 16, -C*H*=CHCN) ppm. Found: C 48.81, H 4.06, N 13.99%. Calculated for $C_8H_8N_2S_2$: C 48.97, H 4.08, N 14.28%.

2-Cyanomethyl-1,3-dithiane (23).[12] To a stirred solution of the sulfone **1** (1.93 g, 10 mmol) in chloroform (30 mL) was added, in one portion, a mixture of 1,3-propanedithiol (1.08 g, 10 mmol) and triethylamine (4.04 g, 4 eq.). After 2 hr the reaction mixture was diluted with chloroform and washed with aqueous hydrochloric acid and with aqueous sodium hydroxide solution. After drying, evaporation of solvent yielded a product mixture consisting largely of the dithiane **23** as an oil which was distilled, b. p. 215 °C/0.2mm Hg, to give pure material as an oil (0.84 g, 53%), ν_{max} (L) 2225 and 1415 cm^{-1}, δ_H (60 MHz) 2.00 (2H, m, -SCH$_2$C*H*$_2$CH$_2$S-), 2.83 (2H, d, *J* 7, -C*H*$_2$CN), 2.90 (4H, m, -SC*H*$_2$CH$_2$C*H*$_2$S-) and 4.16 (1H, t, *J* 7, -C*H*-CH$_2$CN) ppm. Found: C 45.32, H 5.93, N 8.68%. Calculated for $C_6H_9NS_2$: C 45.28, H 5.66, N 8.80%.

(*E*,*E*)-4,8-Dithiaundeca-2,9-diene-1,11-dinitrile (24). To a stirred solution of the sulfone **1** (1.93 g, 10 mmol) in chloroform (30 mL) was added 1,3-propanedithiol (0.48 g, 5 mmol). Triethylamine (1.01 g, 1 eq.) was added dropwise during 0.5 hr. After a further 1.5 hr the reaction mixture was diluted with chloroform and washed with aqueous hydrochloric acid and with aqueous sodium hydroxide solution. After drying, evaporation of solvent yielded crude dithiaundecadiene **24** as an oil (1.58 g, 94%) that could not be distilled without decomposition but which was purified by column chromatography over silica gel using an ethyl acetate – hexane gradient as eluent, ν_{max} (L) 2210, 1570, 940 and 860 cm^{-1}, δ_H (60 MHz) 2.1 (2H, m, -SCH$_2$C*H*$_2$CH$_2$S-), 2.94 (4H, m, -SC*H*$_2$CH$_2$C*H*$_2$S-), 5.43 (2H, d, *J* 16, -CH=C*H*CN) and 7.60 (2H, d, *J* 16, -C*H*=CHCN) ppm. Found: C 51.21, H 4.87, N 13.14%. Calculated for $C_9H_{10}N_2S_2$: C 51.43, H 4.76, N 13.33%.

(*E*)-3-(2-Hydroxyethyl)thioprop-2-enenitrile (25). To a stirred solution of the sulfone **1** (1.93 g, 10 mmol) in chloroform (30 mL) was added, in one portion, a mixture of thioethanol (0.78 g, 10 mmol) and triethylamine (1.01 g, 4 eq.). After 1 hr the reaction mixture was diluted with chloroform and washed with aqueous hydrochloric acid and with aqueous sodium hydroxide solution. After drying, evaporation of solvent yielded an oily product which was distilled to give the pure nitrile **25** as an oil (0.60 g, 47%), b. p. 115 °C/0.4mm Hg, ν_{max} (L) 3460, 2220 and 1570 cm^{-1}, δ_H (60 MHz) 2.40 (1H, br s, exch. D$_2$O, -O*H*), 2.93 (2H, t, *J* 7, -C*H*$_2$S-), 3.80 (2H, t, *J* 7, -C*H*$_2$OH), 5.20 (1H, d, *J* 16, -CH=C*H*CN) and 7.30 (1H, d, *J* 16, -C*H*=CHCN) ppm. Found: C 46.65, H 5.32, N 10.58%. Calculated for C_5H_7NOS: C 46.51, H 5.43, N 10.85%.

(*E*)-3-Ethoxyprop-2-enenitrile (27).[13] Dry, powdered sodium ethoxide (1.02 g, 1.5 eq.) was added to a stirred solution of the sulfone **1** (1.93 g) in dry THF (30 mL). After 4 hr the reaction mixture was diluted with ether and the extract was washed with water, dried, evaporated and distilled to give the enol ether **27** (0.5 g, 51%), b. p. 68 °C/20 mm Hg, ν_{max} (L) 2200, 1637 and 956 cm^{-1}, δ_H (60 MHz) 1.35 (3H, t, *J* 7, -CH$_2$C*H*$_3$), 3.93 (2H, q, *J* 7, -OC*H*$_2$CH$_3$), 4.67 (1H, d, *J* 13.5, -CH=C*H*CN) and 7.23 (1H, d, *J* 13.5, -C*H*=CHCN) ppm. Found: C 61.55, H 7.52, N 14.01%. Calculated for C_5H_7NO: C 61.86, H 7.22, N 14.43%.

3,3-Diethoxypropanenitrile (28). Dry, powdered sodium ethoxide (12.24 g, 6 eq.) was added to a stirred solution of the sulfone **1** (5.79 g, 30 mmol) in dry THF (100 mL). After 4 hr the reaction mixture was diluted with ether and the extract was washed with water, dried, evaporated and distilled to give the acetal **28** (3.08 g, 72%), b. p. 82 ^{o}C/20 mm Hg, ν_{max} (L) 2260 and 1070 cm^{-1}, δ_H (60 MHz) 1.30 (6H, t, *J* 7, -CH_2CH_3), 2.76 (2H, d, *J* 6, -CH_2CN), 3.76 (2H, q, *J* 7, -OCH_2CH_3), 3.80 (2H, q, *J* 7, -OCH_2CH_3) and 4.94 (1H, t, *J* 6, -$CHCH_2$-) ppm. Found: C 58.57, H 9.26, N 9.70%. Calculated for $C_7H_{13}NO_2$: C 58.74, H 9.09, N 9.79%.

(*E*)-3-Phenoxyprop-2-enenitrile (29). [16] Freshly prepared, powdered sodium phenoxide (1.74 g, 1.5 eq.) was added portionwise to a stirred solution of the sulfone **1** (1.93 g, 10 mmol) in dry THF (30 mL). After 3 hr the reaction mixture was diluted with ether and the extract was washed with water, dried, evaporated and distilled to give the enol ether **29** (0.88 g, 60%), b. p. 128-130 ^{o}C/20 mm Hg, (*lit*.[16] b. p. 102-104 ^{o}C/2mm Hg), m. p. 45-47 ^{o}C, ν_{max} (L) 2210, 1620 and 1210 cm^{-1}, δ_H (60 MHz) 4.96 (1H, d, *J* 13, -CH=C*H*CN), 6.90-7.43 (5H, m, ArH) and 7.43 (1H, d, *J* 13, -C*H*=CHCN) ppm. Found: C 74.13, H 4.73, N 9.81%. Calculated for C_9H_7NO: C 74.48, H 4.87, N 9.65%.

(*E*)-3-(2-Methylprop-2-enoxy)prop-2-enenitrile (30). To 2-methylprop-2-enol (2.38 g, 33 mmol) in THF (10 mL) was added sodium hydride (60%, 1.32 g, 1.1 eq.). After 1 hr the resulting solution of alkoxide was added to a stirred solution of the sulfone **1** (5.76 g, 30 mmol) in THF (100 mL). After a further 4 hr the mixture was worked up in the usual way to afford the enol ether **30** (1.95 g, 53%), b. p. 92-93 ^{o}C/20 mm Hg, ν_{max} (L) 2220, 1630, 1620 and 1200 cm^{-1}, δ_H (60 MHz) 1.76 (3H, s, -CH_3), 4.30 (2H, s, -C=C(CH_3)CH_2O-), 4.70 (1H, d, *J* 13, -CH=C*H*CN), 5.03 (2H, br s, -C=CH_2) and 7.16 (1H, d, *J* 13, -C*H*=CHCN) ppm. Found: C 68.58, H 7.54, N 11.00%. Calculated for C_7H_9NO: C 68.29, H 7.32, N 11.38%.

(*E*)-3-(Prop-2-ynyloxy)prop-2-enenitrile (31). To prop-2-ynol (0.56 g, 10 mmol) in THF (10 mL) was added sodium hydride (60%, 0.4 g, 1.1 eq.). After 1 hr the resulting solution of alkoxide was added to a stirred solution of the sulfone **1** (1.93 g, 10 mmol) in THF (30 mL). After a further 4 hr the mixture was worked up in the usual way to afford the enol ether **31** (0.67 g, 63%), b. p. 98 ^{o}C/20 mm Hg, m. p. 24-25 ^{o}C, ν_{max} (L) 3280, 2220, 2120, 1620 and 1170 cm^{-1}, δ_H (60 MHz) 2.66 (1H, t, *J* 2, -CC*H*), 4.54 (2H, d, *J* 2, -CCCH_2-), 4.83 (1H, d, *J* 13, -CH=C*H*CN) and 7.20 (1H, d, *J* 13, -C*H*=CHCN) ppm. Found: C 67.38, H 4.73, N 13.15%. Calculated for C_6H_5NO: C 67.29, H 4.67, N 13.08%.

(*E*)-Pent-2-enenitrile (32). To a solution of the sulfone **1** (1.93 g, 10 mmol) in THF (40 mL) at 0 ^{o}C under N_2 was added dropwise ethylmagnesium bromide (0.67M in THF, 19.4 mL, 1.3 eq.). The reaction mixture was then permitted to warm up to room temperature and stirred for a further 2 hr. THF was evaporated, the residue was taken up with ether and the extract was washed with dilute sodium hydroxide solution and dried. Evaporation of solvent followed by distillation afforded the nitrile **32** (0.46 g, 57%), b. p. 55 ^{o}C/30mm Hg, ν_{max} (L) 2970, 2220, 1630 and 970 cm^{-1}, δ_H (60 MHz) 1.05 (3H, t, *J* 7, CH_3-), 2.23 (2H, dq, *J* 7 and 2, CH_3CH_2C-), 5.23 (1H, dt, *J* 17 and 2, -CH=C*H*CN) and 6.66 (1H, dt, *J* 17 and 7, -C*H*=CHCN) ppm, spectroscopically identical with an authentic specimen.[17]

(*E*)-3-Cyclohexylprop-2-enenitrile (33). [18] To a solution of the sulfone **1** (2.5 g, 13 mmol) in THF (30 mL) at 0 ^{o}C under N_2 was added dropwise cyclohexylmagnesium chloride (0.84M in THF, 17.0 mL, 1.1 eq.). The reaction mixture was then permitted to warm up to room temperature and stirred for a further 1 hr. THF was evaporated, the residue was taken up with ether and the extract was washed with dilute sodium hydroxide solution and dried. Evaporation of solvent followed by distillation afforded the nitrile **34** (1.03 g, 59%), b. p. 69 ^{o}C/0.3mm Hg, (*lit*.[18] b. p. 87 ^{o}C/0.2mm Hg), ν_{max} (L) 2220, 1625, 1445 and 960 cm^{-1}, δ_H (60 MHz) 1.0-2.0 (11H, m), 5.36 (1H, d, *J* 17, -CH=C*H*CN) and 6.76 (1H, dd, *J* 17 and 7, -C*H*=CHCN) ppm.

(*E*)-3-Phenylprop-2-enenitrile (34). To a solution of the sulfone **1** (2.5 g, 13 mmol) in THF (75 mL) at 0 ^{o}C under N_2 was added dropwise phenylmagnesium bromide (0.89M in THF, 16.0 mL, 1.1 eq.). The reaction mixture was then permitted to warm up to room temperature and stirred for a further 2 hr. THF was evaporated, the residue was taken up with ether and the extract was washed with dilute sodium hydroxide solution and dried. Evaporation of solvent followed by distillation afforded the nitrile **33** (1.31 g, 78%), b. p. 120-123 ^{o}C/20mm Hg, ν_{max} (L) 2220, 1632, 970, 750 and 690 cm^{-1}, δ_H (60 MHz) 5.70 (1H, d, *J* 17, -CH=C*H*CN) 7.20 (1H, d, *J* 17, -C*H*=CHCN) and 7.3 (5H, m, ArH) ppm, spectroscopically identical with an authentic specimen.

(*E*)-Non-2-ene-4-ynenitrile (35). 1-Hexyne (1.0 g, 12.2 mmol) in THF (20 mL) was treated at 0 ^{o}C under N_2 with a solution of ethylmagnesium bromide (1M in THF, 12 mL, 0.99 eq.). After 20 min a solution of the sulfone **1** (2.35 g, 12.2 mmol) in THF (40 mL) was added dropwise and the mixture was stirred for a further 2 hr. THF was evaporated, the residue was taken up with ether and the extract was washed with dilute sodium hydroxide solution and dried. Evaporation of solvent followed by distillation afforded the nitrile **35** (1.1 g, 68%), b. p. 70-72 ^{o}C/20 mm Hg, ν_{max} (L) 2340, 2200, 1600 and 690 cm^{-1}, δ_H (60 MHz) 0.98 (3H, t, *J* 6, -C*H*$_3$), 1.25-1.65 (4H, m, -C*H*$_2$C*H*$_2$-), 2.35 (2H, m, -C*H*$_2$CC-), 5.66 (1H, d, *J* 17, -CH=C*H*CN) and 6.55 (1H, dt, *J* 17 and 2, -C*H*=CHCN) ppm. Found: C 80.94, H 8.13, N 10.75%. Calculated for $C_9H_{11}N$: C 81.20, H 8.27, N 10.53%.

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