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 reported1 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 unstable² species, existing³ in  
interstellar dust clouds and in the atmosphere of Titan, the largest moon of Saturn.

![Figure 1](image-url)
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 \textit{ab initio}. Nesmeyanov \textit{et al}.\textsuperscript{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 \textit{et al}.\textsuperscript{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 Nesmoyanov, this result was interpreted as reflecting the comparable stabilities of each of the intermediate carbanions 13 and 14 (pKₐ for H₃CSO₂Ph = 29; pKₐ for H₃CCN = 31; both values are for DMSO solutions).

The same group 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 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](image)

**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

![Chemical structures](image)

**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 thienol 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 Prange14 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.

\[ \text{RO} = \text{EtO} \]
\[ \text{CN} = \text{CN} \]
\[ \text{R} = \text{Et} \]
\[ \text{R} = \text{Ph} \]
\[ \text{R} = \text{H}_{2}C=\text{CH(Me)CH}_{2} \]
\[ \text{R} = \text{HC}≡\text{CCH}_{2} \]

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 synthesised15 via addition of propargyl alcohol to cyanoacetylene in the presence of either K₂CO₃ (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 polymerisation1 was formed. However, the addition
of Grignard reagents to (E)-phenylsulfonylprop-2-enenitrile 1 proceeded smoothly at the sulfonyle 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.

![Figure 7](image-url)

**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 benzenesulfonic 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.** 1H NMR spectra were obtained for solutions in CDCl₃ 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 60F₂₅₄ 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\textsuperscript{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 distillated to give the product 19 as an oil (2.53 g, 76%), b. p. 98-102 °C/0.2 mm Hg, \[\text{litr.}\,\text{9} \,\text{b. p.} \,\text{95-103} \,\text{o} \,\text{C}/0.1 \,\text{mm Hg}], \nu_{\max} (L) 2220, 1565, 750 and 690 cm\(^{-1}\), \(\delta_H\) (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\(_9\)H\(_7\)NS: 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%) \[\text{litr.}\,\text{10} \,\text{an oil}, \,\text{b. p.} \,\text{165} \,\text{o} \,\text{C}/0.2 \,\text{mm Hg}, \nu_{\max} (L) 2225, 1575, 750 and 690 cm\(^{-1}\), \(\delta_H\) (60 MHz) 2.66 (2H, d, \(J 7, -CH\_2CN\)), 4.38 (1H, t, \(J 7, -CH\_CH\_2CN\)) and 7.1-7.5 (10H, m, ArH) 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). \textsuperscript{11} To a stirred solution of the sulfone 1 (1.93 g, 10 mmol) in chloroform (30 mL) was added 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/0.2 mm Hg, \nu_{\max} (L) 2230 and 1415 cm\(^{-1}\), \(\delta_H\) (60 MHz) 2.80 (2H, d, \(J 6, -CH\_2CN\)), 3.30 (4H, s, \(-SC\_H\_2CH\_2S-)\) and 4.60 (1H, t, \(J 6, -CH-CH\_2CN\)) ppm. Found: C 41.28, H 4.67, N 9.51%. Calculated for C\(_5\)H\(_7\)NS\(_2\): 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 dithiadiene 22 as a solid (0.87 g, 89%), m. p. 116-
117 °C, $\nu_{\text{max}}$ (N) 2205, 1565, 950 and 855 cm$^{-1}$, $\delta_{\text{H}}$ (60 MHz) 3.26 (4H, s, -SCH$_2$CH$_2$S-), 5.46 (2H, d, $J$ 16, -CH=CHCN) and 7.46 (2H, d, $J$ 16, -CH=CHCN) ppm. Found: C 48.81, H 4.06, N 13.99%. Calculated for C$_3$H$_4$N$_2$S$_2$: C 48.97, H 4.08, N 14.28%.

2-Cyanomethyl-1,3-dithiane (23). To a stirred solution of the sulfone I (1.93 g, 10 mmol) in chloroform (30 mL) was added, in one portion, a mixture of 1,3-propanedithiol (0.84 g, 10 mmol) and triethylamine (0.78 g, 10 mmol) and triethylamine (0.84 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%), $\nu_{\text{max}}$ (L) 2225 and 1415 cm$^{-1}$, $\delta_{\text{H}}$ (60 MHz) 2.00 (2H, m, -SCH$_2$CH$_2$CH$_2$S-), 2.83 (2H, d, $J$ 7, -CH$_3$CN), 2.90 (4H, m, -SCH$_2$CH$_2$CH$_2$S-) and 4.16 (1H, t, $J$ 7, -CH=CHCN) ppm. Found: C 45.32, H 5.93, N 8.68%. Calculated for C$_4$H$_7$NS$_2$: C 45.28, H 5.66, N 8.80%.

(E,E)-4,8-Dithiaundecadiene-2,9-diene-1,11-dinitrile (24). To a stirred solution of the sulfone I (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 drop wise 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, $\nu_{\text{max}}$ (L) 2210, 1570, 940 and 860 cm$^{-1}$, $\delta_{\text{H}}$ (60 MHz) 2.1 (2H, m, -SCH$_2$CH$_2$CH$_2$S-), 2.94 (4H, m, -SCH$_2$CH$_2$CH$_2$S-) and 5.43 (2H, d, $J$ 16, -CH=CHCN) and 7.60 (2H, d, $J$ 16, -CH=CHCN) ppm. Found: C 51.21, H 4.87, N 13.14%. Calculated for C$_8$H$_{10}$N$_2$S$_2$: C 51.43, H 4.76, N 13.33%.

(E)-3-(2-Hydroxyethyl)thioprop-2-enenitrile (25). To a stirred solution of the sulfone I (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 (0.84 g, 1 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, $\nu_{\text{max}}$ (L) 3460, 2220 and 1570 cm$^{-1}$, $\delta_{\text{H}}$ (60 MHz) 2.40 (1H, br s, exch. D$_2$O, -OH), 2.93 (2H, t, $J$ 7, -CH$_2$S-) and 3.80 (2H, t, $J$ 7, -CH$_2$OH) ppm. Found: C 46.65, H 5.32, N 10.58%. Calculated for C$_5$H$_7$NS: C 46.51, H 5.43, N 10.85%.

(E)-3-Ethoxyprop-2-enenitrile (27). Dry, powdered sodium ethoxide (1.02 g, 1.5 eq.) was added to a stirred solution of the sulfone I (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, $\nu_{\text{max}}$ (L) 2200, 1637 and 956 cm$^{-1}$, $\delta_{\text{H}}$ (60 MHz) 1.35 (3H, t, $J$ 7, -CH$_2$CH$_3$), 3.93 (2H, q, $J$ 7, -OCH$_2$CH$_3$), 4.67 (1H, d, $J$ 13.5, -CH=CHCN) and 7.23 (1H, d, $J$ 13.5, -CH=CHCN) ppm. Found: C 61.55, H 7.52, N 14.01%. Calculated for C$_5$H$_7$NO: 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 °C/20 mm Hg, νmax (L) 2260 and 1070 cm⁻¹, δH (60 MHz) 1.30 (6H, t, J 7, -CH3), 4.30 (2H, s, -C=CH2CH2O-) ppm. Found: C 58.74, H 9.26, N 9.70%. Calculated for C₃H₁₃NO₂: C 58.74, H 9.09, N 9.79%.

(E)-3-Phenoxyprop-2-enenitrile (29). ⁶ 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 °C/20 mm Hg, (lit.⁶ b. p. 102-104 °C/2 mm Hg), m. p. 45-47 °C, νmax (L) 2210, 1620 and 1210 cm⁻¹, δH (60 MHz) 4.96 (1H, d, J 13, -CH=CHCN), 6.90-7.43 (5H, m, ArH) and 7.43 (1H, d, J 13, -CH=CHCN) ppm. Found: C 74.13, H 4.73, N 9.81%. Calculated for C₉H₁₅NO: 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 °C/20 mm Hg, νmax (L) 2220, 1630, 1620 and 1200 cm⁻¹, δH (60 MHz) 1.76 (3H, s, -CH3), 4.30 (2H, s, -C=(CH3)CH2O-), 4.70 (1H, d, J 13, -CH=CHCN), 5.03 (2H, br s, -C=CH2) and 7.16 (1H, d, J 13, -CH=CHCN) ppm. Found: C 68.58, H 7.54, N 11.00%. Calculated for C₆H₁₂NO: C 68.29, H 7.32, N 11.38%.

(E)-3-(2-Methylprop-2-enyl)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 °C/20 mm Hg, m. p. 24-25 °C, νmax (L) 3280, 2220, 2120, 1620 and 1170 cm⁻¹, δH (60 MHz) 2.66 (1H, t, J 2, -CCCH), 4.54 (2H, d, J 2, -CCCH2-), 4.83 (1H, d, J 13, -CH=CH-CN) and 7.20 (1H, d, J 13, -CH=CH-CN) ppm. Found: C 67.38, H 4.73, N 13.15%. Calculated for C₆H₁₂NO: C 66.29, 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 °C under N₂ 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 °C/30 mm Hg, νmax (L) 2970, 2220, 1630 and 970 cm⁻¹, δH (60 MHz) 1.05 (3H, t, J 7, CH3-), 2.23 (2H, dq, J 7 and 2, CH3CH2C-), 5.23 (1H, dt, J 17 and 2, -CH=CH-CN) and 6.66 (1H, dt, J 17 and 7, -CH=CH-CN) ppm, spectroscopically identical with an authentic specimen.¹⁷
(E)-3-Cyclohexylprop-2-enenitrile (33).\textsuperscript{18} To a solution of the sulfone 1 (2.5 g, 13 mmol) in THF (30 mL) at 0 °C under N\textsubscript{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 °C/0.3mm Hg, \textit{lit.}\textsuperscript{18} b. p. 87 °C/0.2mm Hg, \(\nu_{\text{max}}\) (L) 2220, 1625, 1445 and 960 cm\textsuperscript{-1}, \(\delta_{\text{H}}\) (60 MHz) 1.0-2.0 (11H, m), 5.36 (1H, d, \(J\) 17, -CH=CHCN) and 6.76 (1H, dd, \(J\) 17 and 7, -CH=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 °C under N\textsubscript{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 °C/20mm Hg, \(\nu_{\text{max}}\) (L) 2220, 1632, 970, 750 and 690 cm\textsuperscript{-1}, \(\delta_{\text{H}}\) (60 MHz) 5.70 (1H, d, \(J\) 17, -CH=CHCN) 7.20 (1H, d, \(J\) 17, -CH=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 °C 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 °C/20 mm Hg, \(\nu_{\text{max}}\) (L) 2340, 2200, 1600 and 690 cm\textsuperscript{-1}, \(\delta_{\text{H}}\) (60 MHz) 0.98 (3H, t, \(J\) 6, -CH\textsubscript{2}H), 1.25-1.65 (4H, m, -CH\textsubscript{2}CH\textsubscript{2}H\textsubscript{2}-), 2.35 (2H, m, -CH\textsubscript{2}CC-), 5.66 (1H, d, \(J\) 17, -CH=CHCN) and 6.55 (1H, dt, \(J\) 17 and 2, -CH=CHCN) ppm. Found: C 80.94, H 8.13, N 10.75%. Calculated for C\textsubscript{9}H\textsubscript{11}N: C 81.20, H 8.27, N 10.53%.

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References


