

Reaction of Vinyl Sulphone with α -Metallated Nitriles

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Vinyl sulphones (1) were subjected to nucleophilic addition by α -lithionitriles (2) and gave cyclized products, 3-oxothian 1,1-dioxides (3) or cyclopropane derivatives (4), in satisfactory yields according to the substituents on the reagents. The cyclopropanation reactions could be extended to the formation of cyclopropyl sulphides (12)—(16) in good yields.

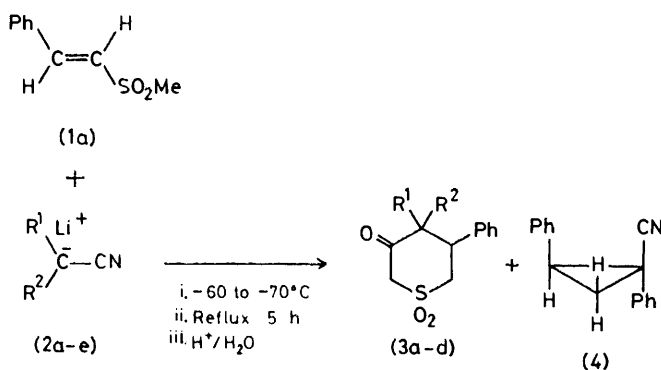
VINYL sulphones, being good Michael acceptors, have attracted an increasing amount of attention as they are useful reagents for carbon-carbon bond formation. For example, they give Michael addition products with a number of nucleophiles such as enolate anions and organometallic reagents in good yields,¹⁻⁴ and the adducts are often subjected to reductive elimination of the sulphonyl group. However, the further synthetic applications of the intermediate carbanions formed in such reactions have not been studied so extensively. We may expect intramolecular reaction of the carbanions if an appropriate functional group can be incorporated into either or both of the sulphones and the addends.

We have now studied the reaction of vinyl sulphones with α -metallated nitriles, whose nucleophilic addition to the former gave rise to intramolecular cyclization forming either oxothian or cyclopropane derivatives in good yields. In the reactions the sulphonyl group played a dual role, that of electron-withdrawing group and leaving group, and hence the effect of the substituents was remarkable. The present method seems to be superior to similar cyclopropane formations *via* addition-displacement reactions of carbanions with α -halogenones,⁵ vinyl sulphonium salts,⁶ triflones,⁷ and vinyl sulphoximines.⁸

Methyl styryl sulphone (1a) was allowed to react with the α -lithionitriles (2a—d) in THF at -60 to -70 °C and finally under reflux to give the 3-oxothian 1,1-dioxide derivatives (3a—d) in good yields. The products were identified by their spectral data and elemental analyses. The i.r. spectra of the sulphones (3) showed absorption bands in the region 1710 — 1730 cm^{-1} as well as two absorptions at 1110 — 1120 and 1300 — 1310 cm^{-1} due

to the symmetric and asymmetric stretching vibrations of the sulphonyl group. ^1H N.m.r. spectra also support these cyclic structures.

On the other hand, α -lithiophenylacetonitrile (2e) reacted with the sulphone (1a) to give none of the cyclic sulphone corresponding to (3) but instead gave the cyclopropane derivative (4) in 68% yield. The cyclopropane (4) was shown to be a single isomer with the two phenyl groups *trans* to each other.†



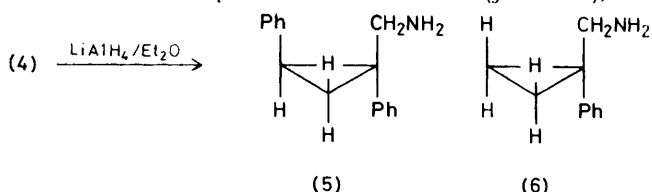
a; $\text{R}^1 = \text{R}^2 = \text{H}$	51%
b; $\text{R}^1 = \text{H}, \text{R}^2 = \text{Me}$	76%
c; $\text{R}^1 = \text{R}^2 = \text{Me}$	80%
d; $\text{R}^1 = \text{H}, \text{R}^2 = \text{Et}$	89%
e; $\text{R}^1 = \text{H}, \text{R}^2 = \text{Ph}$	88%

The possible paths for the reactions described above are shown in the Scheme. In the case of the reaction of the α -lithioaliphatic nitriles (2a—d), the carbanion (7) formed by nucleophilic addition of the nitriles causes intramolecular anion exchange to form the more stable carbanion (8), which undergoes nucleophilic attack at the cyano-group to give the imine (9). Hydrolysis afforded the isolable 3-oxothian 1,1-dioxide (3).

On the other hand, the stability of the carbanion (10) at the position α to the cyano-group is increased by the phenyl substituent in the reaction with α -lithiophenylacetonitrile (2e), and hence intramolecular nucleophilic substitution would occur to eliminate methyl sulphinate anion giving the cyclopropane (4). Thus the nature of the substituents affects the equilibrium among the carbanions (7), (8), and (10), affording two reaction paths.

As an extension of this cyclopropane formation, phenyl

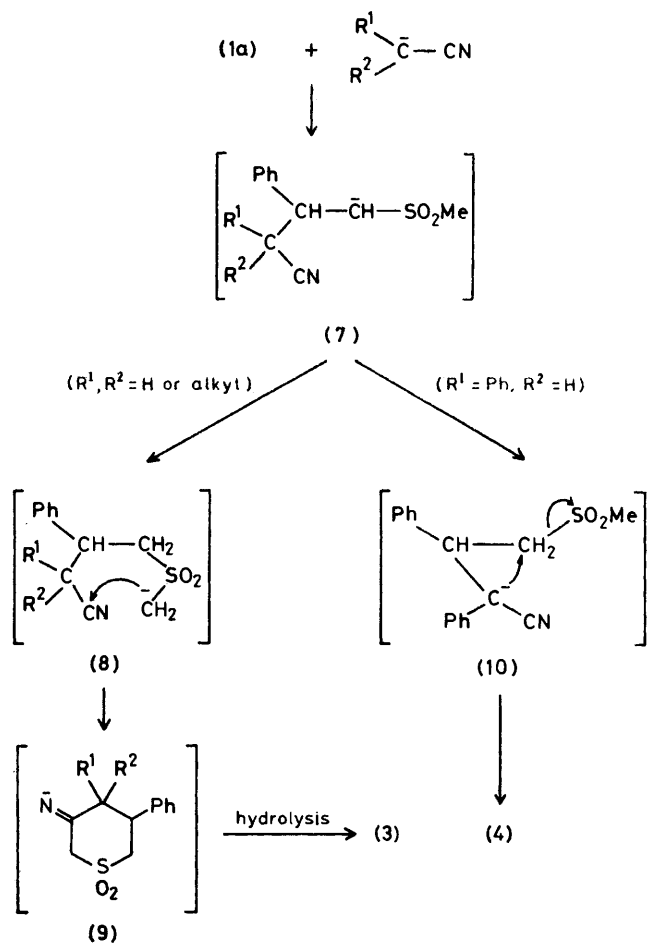
† The structure was determined by comparison of the ^1H n.m.r. spectra of the cyclopropane (5), which is the reduction product of (4), and of the alternatively synthesized cyclopropane (6). While the signal of the exocyclic methylene group of (5) was observed as an AB quartet at δ 2.45 and 2.72 (J 13.6 Hz), the



corresponding protons of (6) show a singlet at δ 2.77. Therefore the exocyclic methylene protons of (5) are considered to be subjected to the weak diamagnetic shielding effect of the *cis* vicinal phenyl group. Such a shielding effect caused by aromatic rings in cyclopropanes is known.⁹ Procedures for the synthesis of (5) and (6) are included in the Experimental section.

vinyl sulphone derivatives were allowed to react with α -lithionitriles, when cyclopropanation reactions exclusively were observed, as expected. Phenyl styryl sulphone (1b) reacted with α -lithiophenylacetonitrile

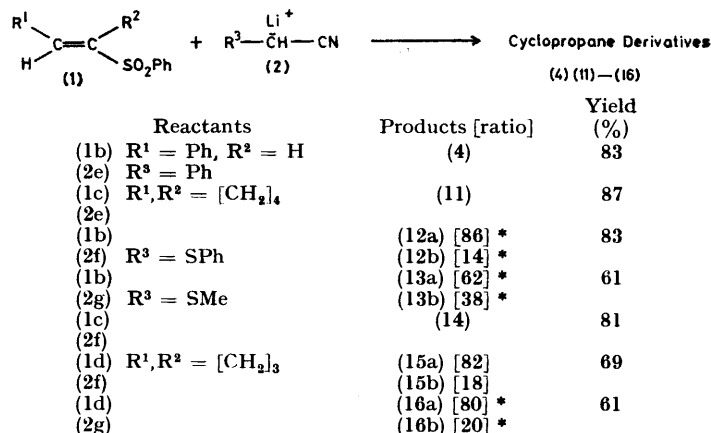
The two stereoisomers, (15a) and (15b), of the bicyclo-[3.1.0]hexane (15) were easily separated by chromatography. Synthesis of cyclopropanes from α -lithionitriles and phenyl vinyl sulphone derivatives



SCHEME

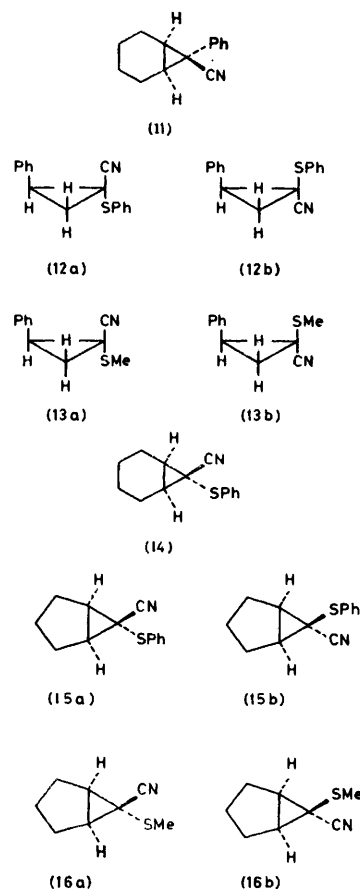
(2e) forming the cyclopropane (4) in a good yield. Similarly the norcarane derivative (11) was obtained in 87% yield when the cyclohexenyl phenyl sulphone (1c) was treated with the lithionitrile (2e). The stereochemistry of (11), a single isomer, was determined on the basis of ¹³C n.m.r. data (see later).

Furthermore, the carbanions (2f and g), generated from α -sulphenylacetonitriles, were employed in the reactions, because introduction of another functional group would not only increase the variety of products but also enable further transformation of the resulting cyclopropanes. When α -lithiophenylthioacetonitrile (2f) and α -lithiomethylthioacetonitrile (2g) were allowed to react with the sulphone (1b), the corresponding phenylthio- (12) and methylthio-cyclopropanes (13) were obtained. The ¹H n.m.r. spectra indicated that the cyclopropanes (12) and (13) were mixtures of two stereoisomers (see Table). Bicyclic cyclopropane derivatives (14)–(16) were also formed from the cycloalkenyl sulphones (1c) and (1d).



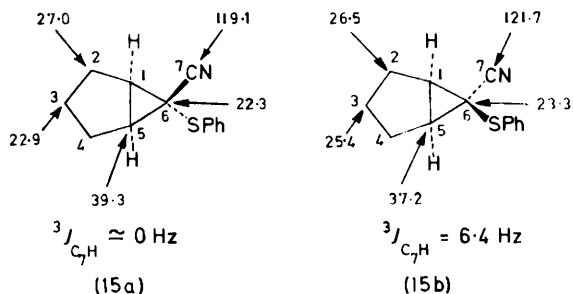
* Ratios determined by n.m.r. spectroscopy.

graphy and the structures were determined by ¹³C n.m.r. spectroscopy. It has been reported¹⁰ that for cyclopropane derivatives, values of ³J_{CH} for *cis*-exocyclic carbon



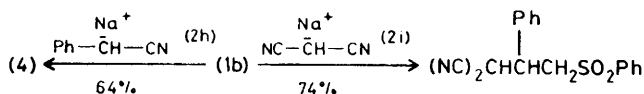
atoms and ring protons are greater than those for *trans*-nuclei. Therefore, the cyanocarbon and the vicinal methine protons of (15a) (³J_{CH} ca. 0 Hz) should have a

trans relationship and those of (15b) ($^3J_{\text{CH}}$ 6.4 Hz) a *cis*. Similarly the stereochemistries of the norcarane derivatives (11) and (14) were found to be identical with the stereochemistry of (15a) ($^3J_{\text{CH}}$ 0 Hz).



^{13}C N.m.r. chemical shifts of compounds (15a) and (15b) (p.p.m. downfield from Me_4Si in CDCl_3 solutions)

Finally we examined the reaction of phenyl styryl sulphone (1b) with α -sodiophenylacetonitrile (2h) and found that the cyclopropanation is not specific to lithionitriles. On the other hand, only the 1:1 adduct was formed in the reaction of the sulphone (1b) with α -sodiomalnonitrile (2i), which is a more stable carbanion. Thus the present cyclopropanation *via* intramolecular displacement is considered to be highly dependent on the nucleophilicity and/or stability of the carbanions.



EXPERIMENTAL

Melting points were determined with a Yamato MP-21 apparatus. ^1H and ^{13}C N.m.r. spectra were recorded with JEOL JNM-PMX-60 and JNM-FT-100 spectrometers respectively. I.r. spectra were obtained on a JASCO IRA-1 spectrometer and mass spectra were recorded on a Hitachi RMU-6E spectrometer at an ionizing voltage of 70 eV.

The vinyl sulphone derivatives (1a—d) were prepared by reported methods¹¹⁻¹³ and the sulphones (1a and b) were checked to be *trans*-isomers by n.m.r. spectroscopy. Commercially available nitriles were used after distillation. Phenylthio- (2f) and methylthio-acetonitrile (2g) were prepared by treating chloroacetonitrile with sodium thiophenolate and sodium methanethiolate respectively. All reactions were carried out under nitrogen using tetrahydrofuran (THF), distilled from sodium metal, as the solvent.

Reactions of Methyl Styryl Sulphone (1a) with α -Lithionitriles (2a—e).—To a stirred solution of *n*-butyl-lithium (6.3 cm³ of 15% hexane solution, 10 mmol) in THF (10 cm³) was added di-isopropylamine (1.4 cm³, 10 mmol) in THF (3 cm³) at 0—5 °C (LDA solution). After stirring for 30 min at the same temperature, the nitrile (2) (10 mmol) in THF (5 cm³) was added to the LDA solution and the stirring was continued at -60 to -70 °C for 2—3 h. Then the sulphone (1a) (1.82 g, 10 mmol) was added and reaction allowed to continue at -60 to -70 °C for 4 h. After standing at room temperature overnight, the solution was refluxed for 5 h and was quenched with water after cooling. The mixture was neutralized with 2*N*-hydrochloric acid,

concentrated, and extracted (CHCl_3). Evaporation of the dried (Na_2SO_4) organic layer left the crude products (3) or (4), which were isolated by chromatography on silica gel and purified by recrystallization or by distillation (Kugelrohr) at the pressure and oven temperature indicated. **3-Oxo-5-phenylthian 1,1-dioxide (3a)** had m.p. 119—121 °C (from benzene-hexane); ν_{max} (Nujol) 1 730 ($\text{C}=\text{O}$), and 1 300 and 1 110 cm^{-1} (SO_2); δ (^{13}C DMSO) 2.3—4.3 (5 H, m, $\text{COCH}_2\text{-CHPhCH}_2\text{SO}_2$), 3.91 (1 H, d, J 13.6 Hz, SO_2CHHCO), 4.75 (1 H, d, J 13.6 Hz, SO_2CHHCO), and 7.2—7.7 (5 H, m, Ph); m/e 224 (M^+) (Found: C, 59.2; H, 5.35; S, 14.15. $\text{C}_{11}\text{H}_{12}\text{O}_3\text{S}$ requires C, 58.90; H, 5.40; S, 14.29%). **4-Methyl-3-oxo-5-phenylthian 1,1-dioxide (3b)** had m.p. 176.5—178 °C (from benzene-hexane); ν_{max} (Nujol) 1 720 ($\text{C}=\text{O}$), and 1 310 and 1 120 cm^{-1} (SO_2); δ (^{13}C DMSO) 0.78 (3 H, d, J 6.4 Hz, Me), 2.9—4.5 (4 H, m, $\text{COCHCHPhCH}_2\text{SO}_2$), 4.10 (1 H, d, J 13.6 Hz, SO_2CHHCO), 4.82 (1 H, d, J 13.6 Hz, SO_2CHHCO), and 7.2—7.7 (5 H, m, Ph); m/e 238 (M^+) (Found: C, 60.55; H, 5.85; S, 13.3. $\text{C}_{12}\text{H}_{14}\text{O}_3\text{S}$ requires C, 60.47; H, 5.93; S, 13.45%). **4,4-Dimethyl-3-oxo-5-phenylthian 1,1-dioxide (3c)** had m.p. 149—150 °C (from benzene-hexane); ν_{max} (Nujol) 1 710 ($\text{C}=\text{O}$), and 1 300 and 1 110 cm^{-1} (SO_2); δ (^{13}C DMSO) 0.86 (3 H, s, Me), 1.17 (3 H, s, Me), 3.0—4.7 (3 H, m, $\text{PhCHCH}_2\text{SO}_2$), 3.98 (1 H, d, J 13.6 Hz, SO_2CHHCO), 4.92 (1 H, d, J 13.6 Hz, $\text{SO}_2\text{-CHHCO}$), and 7.2—7.7 (5 H, m, Ph); m/e 252 (M^+) (Found: C, 61.9; H, 6.35; S, 12.55. $\text{C}_{13}\text{H}_{16}\text{O}_3\text{S}$ requires C, 61.87; H, 6.40; S, 12.70%). **4-Ethyl-3-oxo-5-phenylthian 1,1-dioxide (3d)** had m.p. 162—164 °C (from benzene); ν_{max} (Nujol) 1 710 ($\text{C}=\text{O}$), and 1 305 and 1 110 cm^{-1} (SO_2); δ (^{13}C DMSO) 0.68 (3 H, t, J 6.8 Hz, Me), 1.22 (2 H, dq, J 3.2 and 6.8 Hz, CHCH_2Me), 2.9—4.4 (4 H, m, $\text{COCHCH-PhCH}_2\text{SO}_2$), 4.03 (1 H, J 12.8 Hz, SO_2CHHCO), 4.93 (1 H, J 12.8 Hz, SO_2CHHCO), and 7.0—7.5 (5 H, m, Ph); m/e 252 (M^+) (Found: C, 61.85; H, 6.4; S, 12.7. $\text{C}_{13}\text{H}_{16}\text{O}_3\text{S}$ requires C, 61.87; H, 6.40; S, 12.70%). **r-1-Cyano-1,c-2-diphenylcyclopropane (4)** was an oil; b.p. 160—165 °C at 2 mmHg; ν_{max} (film) 2 240 cm^{-1} ($\text{C}\equiv\text{N}$); δ (CDCl_3) 1.96 (1 H, dd, J 6.0 and 7.4 Hz, CHH), 2.15 (1 H, dd, J 6.0 and 9.0 Hz, CHH), 2.75 (1 H, dd, J 7.4 and 9.0 Hz, CH), and 7.0—7.5 (5 H, m, Ph); m/e 219 (M^+) (Found: C, 87.8; H, 5.8; N, 6.7. $\text{C}_{16}\text{H}_{13}\text{N}$ requires C, 87.62; H, 5.99; N, 6.39%).

Reduction of the Cyclopropane (4) with Lithium Aluminium Hydride.—To a stirred solution of lithium aluminium hydride (49 mg, 1.3 mmol) in anhydrous ether (10 cm³) was added the cyclopropane (4) (280 mg, 1.3 mmol) in ether (6 cm³) at 5—20 °C. After stirring for 5 h and standing overnight at room temperature, the reaction mixture was quenched with water, followed by addition of aqueous sodium potassium tartarate (1.0 g in 5 cm³ of water). The organic layer was extracted (ether), dried (Na_2SO_4), and concentrated *in vacuo* to give a colourless oil. Chromatography on silica gel afforded *r*-1-aminomethyl-1,c-2-diphenylcyclopropane (5) (220 mg, 76%) which was eluted with CHCl_3 ; b.p. 125—130 °C at 1 mmHg; ν_{max} (film) 3 200—3 400 cm^{-1} (NH_2); δ (CDCl_3) 0.97 (2 H, s, NH_2), 1.31 (2 H, d, J 7.2 Hz, endocyclic CH_2), 2.45 (1 H, d, J 13.6 Hz, exocyclic CHH), 2.48 (1 H, t, J 7.2 Hz, CH), 2.72 (1 H, d, J 13.6 Hz, exocyclic CHH), and 7.0—7.6 (10 H, m, 2 Ph) [addition of D_2O caused the signal at δ 0.97 to disappear]; m/e 223 (M^+) (Found: C, 85.95; H, 7.55; N, 6.45. $\text{C}_{16}\text{H}_{17}\text{N}$ requires C, 86.04; H, 7.69; N, 6.27%).

Preparation of the Cyclopropane (6).—To a stirred solution of lithium aluminium hydride (93 mg, 2.4 mmol) in an-

hydrocyclo ether (10 cm³) was added 1-cyano-1-phenylcyclopropane **14** (350 mg, 2.4 mmol) in ether (12 cm³) at 5–20 °C. Work-up as above gave an oil (350 mg), whose distillation afforded 1-aminomethyl-1-phenylcyclopropane (**6**) (290 mg, 83%); b.p. 73–78 °C at 1 mmHg; ν_{\max} (film) 3 200–3 500 cm⁻¹ (NH₂); δ (CDCl₃) 0.7–0.9 (4 H, m, CH₂CH₂), 1.30 (2 H, s, NH₂), 2.77 (2 H, s, exocyclic CH₂), and 7.0–7.5 (5 H, m, Ph) [addition of D₂O caused the signal at δ 1.30 to disappear]; m/e 147 (M^+) [Found (picrate): C, 51.0; H, 4.45; N, 15.05. C₁₆H₁₆N₄O₇ requires C, 51.06; H, 4.29; N, 14.89%].

Reactions of Phenyl Vinyl Sulphone Derivatives (1b–d) with α -Lithionitriles (2e–g).—A solution of LDA was prepared as previously, and the nitriles were metallated at –60 to –70 °C except phenylacetonitrile which was metallated at 0–5 °C. An equimolar amount of the sulphone (**1**) in THF was added to the solution and the stirring was continued for 30 min at the temperature of the above metallation. The mixture was allowed to stand overnight at room temperature and then refluxed for 5 h. Work-up as previously gave the cyclopropanes (**4**) and (**11**)–(**16**). endo-7-Cyano-exo-7-phenylnorcarane (**11**) was an oil; b.p. 115–122 °C at 1 mmHg; ν_{\max} (film) 2 240 cm⁻¹ (C≡N); δ (CDCl₃) 1.0–2.3 (10 H, m, 4 CH₂ and 2 CH), and 6.9–7.7 (5 H, m, Ph); δ_C (CDCl₃) 20.5 (t, ¹J_{CH} 129.4 Hz, CH₂), 25.3 (s, PhCCN), 28.3 (d, ¹J_{CH} 167.2 Hz, CH), 120.0 (s, CN), and 125.1, 127.1, 128.8, and 137.9 (aromatic); m/e 197 (M^+) (Found: C, 85.25; H, 7.65; N, 7.2. C₁₄H₁₅N requires C, 85.22; H, 7.68; N, 7.10%). r-1-Cyano-c-2-phenyl-1-phenylthiocyclopropane (**12a**) and its isomer (**12b**) were obtained as a 86 : 14 mixture (n.m.r.); b.p. 180–184 °C at 1 mmHg; ν_{\max} (film) 2 240 cm⁻¹ (C≡N); δ (CDCl₃) 1.76 (dd, J 9.1 and 6.2 Hz, *cis*-CHH), 1.80 (dd, J 7.3 and 6.0 Hz, *trans*-CHH), 1.98 (dd, J 9.3 and 6.2 Hz, *cis*-CHH), 2.06 (dd, J 9.5 and 6.0 Hz, *trans*-CHH), 2.84 (dd, J 9.5 and 7.3 Hz, *trans*-CH), and 3.12 (dd, J 9.3 and 9.1 Hz, *cis*-CH); m/e 251 (M^+) (Found: C, 76.15; H, 5.25; N, 5.5; S, 13.1. C₁₆H₁₃NS requires C, 76.45; H, 5.22; N, 5.57; S, 12.75%). r-1-Cyano-1-methylthio-c-2-phenylcyclopropane (**13a**) and its isomer (**13b**) were isolated as a 62 : 38 mixture (n.m.r.); b.p. 150–155 °C at 1 mmHg; ν_{\max} (film) 2 240 cm⁻¹ (C≡N); δ (CDCl₃) 1.67 (dd, J 8.0 and 6.0 Hz, *cis*-CHH), 1.70 (dd, J 7.5 and 6.0 Hz, *trans*-CHH), 1.97 (dd, J 9.6 and 6.0 Hz, *cis*-CHH), 1.98 (s, *cis*-Me), 2.00 (dd, J 9.4 and 6.0 Hz, *trans*-CHH), 2.38 (s, *trans*-Me), 2.74 (dd, J 9.4 and 7.5 Hz, *trans*-CH), and 3.08 (dd, J 9.6 and 8.0 Hz, *cis*-CH); m/e 189 (M^+) (Found: C, 69.4; H, 5.85; N, 7.3; S, 17.15. C₁₁H₁₁NS requires C, 69.79; H, 5.87; N, 7.40; S, 16.94%). endo-7-Cyano-exo-7-phenylthionorcarane (**14**) was an oil; b.p. 145–152 °C at 1 mmHg; ν_{\max} (film) 2 240 cm⁻¹ (C≡N); δ (CDCl₃) 1.0–2.7 (10 H, m, 4 CH₂ and 2 CH) and 7.0–7.7 (5 H, m, Ph); δ_C (CDCl₃) 20.1 and 20.6 (t, ¹J_{CH} 130.0 Hz, respectively, CH₂CH₂), 22.5 (s, PhSCCN), 29.2 (d, ¹J_{CH} 169.7 Hz, CH), 119.5 (s, CN), and 127.3, 129.1, 129.3, and 134.2 (aromatic); m/e 229 (M^+) (Found: C, 73.05; H, 6.5; N, 6.15; S, 13.8. C₁₄H₁₅NS requires C, 73.30; H, 6.61; N, 6.11; S, 13.98%). endo-6-Cyano-exo-6-phenylthiobicyclo[3.1.0]hexane (**15a**) and the exo-endo-isomer (**15b**) were obtained as a mixture and were separated by silica gel chromatography [benzene-hexane (1 : 5) as eluant]. The ratio of (**15a**) to (**15b**) was 82 : 18. The endo-exo-isomer (**15a**) was an oil; b.p. 158–163 °C at 2 mmHg; ν_{\max} (film) 2 240 cm⁻¹ (C≡N); δ (CDCl₃) 1.3–2.3 (8 H, m, 3 CH₂ and 2 CH) and 7.0–7.7 (5 H, m, Ph); m/e 215 (M^+) (Found: C, 72.3; H, 6.15; N, 6.45; S, 14.75. C₁₃H₁₃NS requires C, 72.51; H, 6.10; N, 6.51; S,

14.89%). The exo-endo-isomer (**15b**) had b.p. 150–155 °C at 1 mmHg; ν_{\max} (film) 2 240 cm⁻¹ (C≡N); δ (CDCl₃) 1.6–2.3 (6 H, m, 3 CH₂), 2.3–2.7 (2 H, m, 2 CH), and 7.0–7.7 (5 H, m, Ph); m/e 215 (M^+) (Found: C, 72.65; H, 6.15; N, 6.75%). endo-6-Cyano-6-methylthiobicyclo[3.1.0]hexane (**16a**) and the exo-endo-isomer (**16b**) were obtained as a 4 : 1 mixture (n.m.r.); b.p. 127–128 °C at 18–20 mmHg; ν_{\max} (film) 2 240 cm⁻¹ (C≡N); δ [CDCl₃-benzene (1 : 1)] 1.0–1.8 [7.6 H, m, 3 CH₂ and CH of (**16a**)], 1.95 (0.6 H, s, *endo*-SMe), 2.03 (2.4 H, s, *exo*-SMe), and 2.3–2.5 [0.4 H, m, CH of (**16b**)]; m/e 153 (M^+) (Found: C, 62.25; H, 7.25; N, 9.4. C₈H₁₁NS requires C, 62.69; H, 7.25; N, 9.14%).

Reaction of the Sulphone (1b) with α -Sodiophenylacetonitrile (2h).—Sodium hydride (240 mg of 50% dispersion in mineral oil; 5.0 mmol) was freed of mineral oil by washing and decanting with n-hexane. The system was evacuated to remove the solvent and the vacuum was broken by introduction of nitrogen and subsequent addition of THF (5 cm³). Phenylacetonitrile (580 mg, 5.0 mmol) in THF (10 cm³) was added and stirred at 45–50 °C for 3 h. To the stirred solution was added the sulphone (**1b**) (1.22 g, 5.0 mmol) in THF (7 cm³) at 0–5 °C and the stirring was continued for 15 min. The reaction mixture was allowed to stand overnight, quenched with water, and worked up as previously. The resulting oil was purified on a silica gel column to give the cyclopropane (**4**) (700 mg, 64%) which was eluted with benzene-hexane (1 : 10).

Reaction of the Sulphone (1b) with α -Sodiomalnonitrile (2i).—Sodium hydride (240 mg, 5.0 mmol) was washed and dried as the preceding run. Malononitrile (330 mg, 5.0 mmol) in THF (15 cm³) was added dropwise below 10 °C, and the resulting solution was stirred at room temperature for 1 h. After dropwise addition of the sulphone (**1b**) in THF (20 cm³) at room temperature, the reaction mixture was refluxed for 10 h and was worked up as usual. Concentration followed by addition of a small portion of ether gave 3,3-dicyano-2-phenylethyl phenyl sulphone, which was recrystallized from benzene to afford prisms; m.p. 127–128 °C; ν_{\max} (Nujol) 2 260 cm⁻¹ (C≡N), and 1 290 and 1 140 cm⁻¹ (SO₂); δ (CD₃CN) 3.6–4.2 (3 H, m, PhCHCH₂SO₂), 4.65–4.8 [1 H, m, CH(CN)₂], and 7.2–8.0 (10 H, m, 2 Ph); m/e 310 (M^+) (Found: C, 65.75; H, 4.15; N, 9.1; S, 10.4. C₁₇H₁₄N₂O₂S requires C, 65.78; H, 4.56; N, 9.03; S, 10.33%).

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