Carbon Disulfide as a 2-π Component in Its Cycloaddition with 1-Azirines

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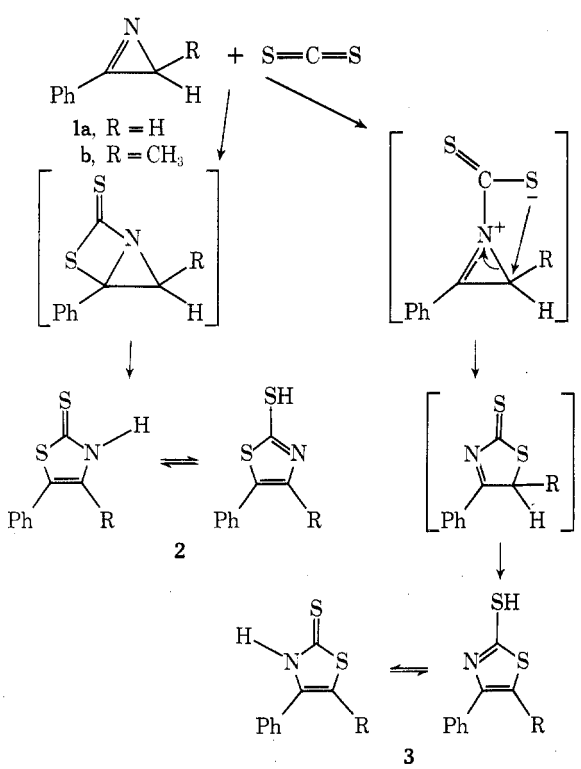
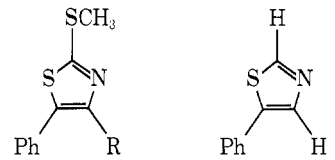
Thermally induced [2 + 2] cycloadditions are rarely encountered. Orbital symmetry analysis reveals that additions of this type that involve relatively low activation energies require special inherent geometric and/or electronic properties of the component(s).[1] The dienophilic and dipolarophilic character of 1-azirines in their thermal cycloadditions has already been established.[2-7] Most reactions of carbon disulfide proceed from an initial nucleophilic attack on carbon.[8-11] The few cycloadditions known are 1,3 dipolar in nature with carbon disulfide as the dipolarophile.[12,13]

We wish to report on the reaction of carbon disulfide with 1-azirines and discuss its mechanistic implications.

When 2-phenyl-1-azirine was dissolved in an excess of carbon disulfide and heated at 100° for 3 hr in a Carius tube, pale yellow needles were obtained, mp 208–209°. Mass spectral data (M^+ at *m/e* 193) and elemental analysis were consistent with the molecular formula $C_9H_7NS_2$, and therefore a 1:1 adduct. The infrared spectrum showed absorptions at 3110 (NH), 1610 (C=C), 1500 (C=S), 1060, 1040 cm^{-1} (C–S–C). Resonances in its ^1H NMR spectrum (in DMSO-d_6) were centered at δ 7.43 (5 H), 7.79 (1 H), and 13.27 (1 H). The broad absorption peak at δ 13.27 underwent rapid exchange with D_2O. Its pulse Fourier transform ^{13}C NMR spectrum (in DMSO-d_6) showed singlets in the phenyl carbon region and a singlet at δ 187.34 which we attribute to a C=S carbon.[14] Collectively, the data are consistent with a thiazole ring system. The adduct could be methylated with methyl iodide in the presence of 1 *M* NaOH. Two plausible structures are **2** and **3**. Compound **2** could conceivably be the eventual result of a [2 + 2] cycloaddition and hydrogen shift(s). Compound **3** (thioenol form) might result from initial nucleophilic attack by the lone pair of the azirine nitrogen on the reactive electrophilic carbon of carbon disulfide followed by 1,3-bond scission, cyclization, and 1,5 sigmatropic rearrangement.



Spectroscopic data did not provide an unambiguous assignment. Structural differentiation came from treatment of the adduct with nitric acid,[15] which gave the known 5-phenylthiazole (**5**), mp 45°.[16] Compound **5** must arise from



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2 by a desulfurization reaction. Our spectroscopic data suggest that **2** exists predominantly in the thioketo form.

The formation of the adduct **2** appears therefore to proceed via a regioselective cycloaddition of carbon disulfide to the π bond of the 1-azirine. To our knowledge this is the first example of such an addition of carbon disulfide to a C=N bond. Whether this combination involves a concerted [$_\pi2_s + _\pi2_a$] pathway or a stepwise mechanism involving a dipolar transition state is not known.

These studies were extended to another representative azirine, 3-methyl-2-phenyl-1-azirine (**1b**). Similar results were observed.

Experimental Section

Reaction of 2-Phenyl-1-azirine (1a) with Carbon Disulfide. A mixture of 0.468 g (4 mmol) of 2-phenyl-1-azirine and 1.00 g (13.2 mmol) of carbon disulfide in a Carius tube was heated at 100° for 3 hr. Excess CS_2 was removed and the resultant solid material crystallized from dichloromethane–ether to give 0.182 g (24%) of **2a** as pale yellow needles: mp 208–209°; ir ν_{max} (Nujol) 3110, 1610, 1500, 1270, 1060, 1040, 750 cm^{-1}; ^1H NMR δ_{Me_4Si} (DMSO-d_6) 7.43 (s, br, 5 H), 7.79 (s, 1 H), 13.27 (s, br, 1 H, exchanges with D_2O); ^{13}C NMR δ_{Me_4Si} (DMSO-d_6) 125.09, 128.06, 129.08, 129.41, 129.89, 187.34; mass spectrum (70 eV) *m/e* 193 (M^+), 161 (M^+ – S), 134 [Ph-(c-C_2S)-H; c-C_2S-azirine ring], 121 (PhCS), 102 (PhC≡CH), 91, 77.

Anal. Calcd for $C_9H_7NS_2$: C, 55.93; H, 3.65; N, 7.25. Found: C, 55.90; H, 4.03; N, 7.34.

Methylation of Thiazole (2a). To a suspension of 0.120 g (0.62 mmol) of **2a** in 6 ml of 1 *M* NaOH was added 0.110 g (0.78 mmol) of methyl iodide in 4 ml of 1 *M* NaOH, and the reaction mixture was stirred at room temperature for 3 hr. The reaction mixture was then brought to pH 7 with dilute acetic acid and then extracted with dichloromethane. The combined extracts were dried (Na_2SO_4) and the solvent was then removed in vacuo. The residual material was purified by preparative layer chromatography using silica gel PF_{254} plates with 50% ether–pentane as the developing solvent. The thiazole thioether (**4a**) was obtained as a pale yellow oil (0.089 g, 70%); ^1H NMR δ_{Me_4Si} ($CDCl_3$) 2.68 (s, 3 H), 7.21–7.48 (m, 5 H), 7.77 (s, 1 H); mass spectrum (70 eV) *m/e* 207.

Anal. Calcd for $C_{10}H_9NS_2$: C, 57.94; H, 4.38; N, 6.76. Found: C, 57.60; H, 4.07; N, 6.67.

Desulfurization of Thiazole (2a). A suspension of 0.150 g (0.78 mmol) of **2a** in 10 ml of water and 4 ml of concentrated nitric acid was stirred at room temperature for 4 hr. The reaction mixture was neutralized with 10 *M* NaOH and extracted with chloroform. The combined extracts were washed with water and dried (Na_2SO_4). Removal of solvent and purification of the product by preparative layer chromatography on aluminum oxide PF_{254} plates with 50% ether–pentane as the developing solvent gave 0.064 (51%) of 5-phenylthiazole (**5**) as white prisms: mp 45° (lit.[16] mp 45–46°); ^1H NMR δ_{Me_4Si} ($CDCl_3$) 7.23–7.58 (m, 5 H), 8.06 (s, 1 H), 8.75 (s, 1 H); mass spectrum (70 eV) *m/e* 161 (M^+), 134 [Ph-(c-C_2S)-H], 102 (PhC≡CH).

Anal. Calcd for C_9H_7NS: C, 67.05; H, 4.38; N, 8.69. Found: C, 66.72; H, 4.15; N, 8.53.

Reaction of 3-Methyl-2-phenyl-1-azirine (1b) with Carbon Disulfide. The azirine **1b** (0.524 g, 4 mmol) was dissolved in car-

bon disulfide (1.00 g, 13.2 mmol) and heated at 100° as described above for **1a**. The thiazole **2b** crystallized from dichloromethane–ether as pale yellow needles (0.324 g, 39%): mp 223–224°; ir ν_{max} (Nujol) 3120, 1605, 1505, 1090, 1075, 710 cm^{-1}; ^1H NMR δ_{Me_4Si} (DMSO-d_6) 2.23 (s, 3 H), 7.36 (s, br, 5 H), 13.09 (s, br, 1 H, exchanges with D_2O); ^{13}C NMR δ_{Me_4Si} (DMSO-d_6) 12.46, 122.50, 127.95, 128.60, 128.97, 134.10, 186.21; mass spectrum (70 eV) *m/e* 207 (M^+), 175 ($M^+ - S$), 148 [Ph-(c-C_2S)-CH_3], 121 (PhCS), 116 ($PhC{\equiv}CCH_3$), 91, 77.

Anal. Calcd for $C_{10}H_9NS_2$: C, 57.94; H, 4.38; N, 6.75. Found: C, 58.00; H, 4.81; N, 6.64.

Methylation of Thiazole 2b. The thiazole **2b** (0.238 g, 1.2 mmol) was methylated with methyl iodide (0.200 g, 1.4 mmol) in 15 ml of 1 *M* NaOH as described above for **2a**. The thiazole thioether **4b** was obtained as a pale yellow oil (0.220 g, 87%); ^1H NMR δ_{Me_4Si} ($CDCl_3$) 2.42 (s, 3 H), 2.64 (s, 3 H), 7.31 (s, br, 5 H); mass spectrum (70 eV) *m/e* 221 (M^+).

Anal. Calcd for $C_{11}H_{11}NS_2$: C, 59.69; H, 5.01; N, 6.33. Found: C, 59.33; H, 4.95; N, 6.16.

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Registry No.—**1a,** 7654-06-0; **1b,** 16205-14-4; **2a,** 25445-02-7; **2b,** 7725-94-2; **4a,** 25445-03-8; **4b,** 54410-38-7; **5,** 1826-13-7; carbon disulfide, 75-15-0.

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Pyrolysis of 2-Alkoxy-1-azetines

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In studies of addition reactions of imino ethers,[1] we were concerned about the conditions necessary for thermal ring opening of 2-alkoxy-1-azetines.[2] We find that complete rearrangement occurs within 8 hr at 200° for 2-methoxy-1-azetines. For azetine **1**, vacuum pyrolysis at 200° for 8 hr results in complete conversion to the unsaturated imino ether **3**. Azetine **4** at 200° for 8 hr gives complete conversion to the analogous unsaturated imino ether **6**. These products can be rationalized by 1,5-hydrogen shifts of the expected intermediates **2** and **5**. Vacuum pyrolysis of azetine **8** under identical conditions gives a 40:60 mixture of isomers **10** and **11** separated by VPC. The compound with the greater retention time was assigned structure **10** by comparison with **3** and **6**. Compound **11** is the product of the alternative 1,5-hydrogen transfer process from **9**. Although **8** readily gives **11**, the analogous product **7** is not formed from azetine **4**. Apparently the *E* isomer of **5**, which would be required for a 1,5-hydrogen shift to produce **7**, is not formed from **4** because of methyl group repulsions.[3] This observation is in good accord with a mechanism involving ring opening of 1-azetines to vinyl imines like **5**, and it eliminates the possibility of a 1,4-diradical intermediate,[2] which would not be expected to specifically give **6** and no **7**.

Paquette and coworkers[2] have reported that ring opening of both (*Z*)- and (*E*)-3,4-diethyl-2-methoxy-1-azetines **12** at 600° give the same mixture of unsaturated imino ethers **14** and **15**. (*Z*)-**12** should open to the *E*, anti vinyl imine **13**, but it should not be capable of 1,5-hydrogen shifts by analogy with our results on pyrolysis of **4**. The