Electrophilic Cleavage of Unsaturated Thiirans

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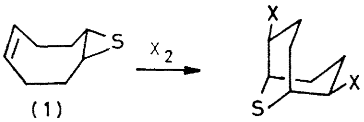
Summary High-yield reactions of unsaturated thiirans with halogens or SCl$_2$ proceed by initial electrophilic attack on sulphur and furnish halogeno-sulphides, in some cases *via* isolable disulphides, thereby providing a novel method of creating an intramolecular disulphide link.

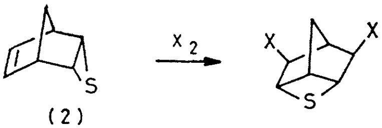
Sulphur-bridged systems are conveniently prepared by the widely applicable condensation[1] of SCl$_2$ with olefins but the halogenolysis[2,3] of unsaturated thiirans as a potential route to dihalogeno-sulphides has not been fully explored. In the latter case, it is not known whether halogen, as an electrophile, first attacks the double bond or the episulphide sulphur atom.

Chlorinolysis of (**1**) and (**2**) furnishes[2,4] respectively, (**3**) and (**6**). Similarly, we have shown that (**1**) reacts[3] at room temperature with Br$_2$ or I$_2$ forming (**4**) (97%) or (**5**) (67%) and that (**2**) undergoes brominolysis to give (**7**)[5] (98%).



(1)

(3) X = Cl
(4) X = Br
(5) X = I

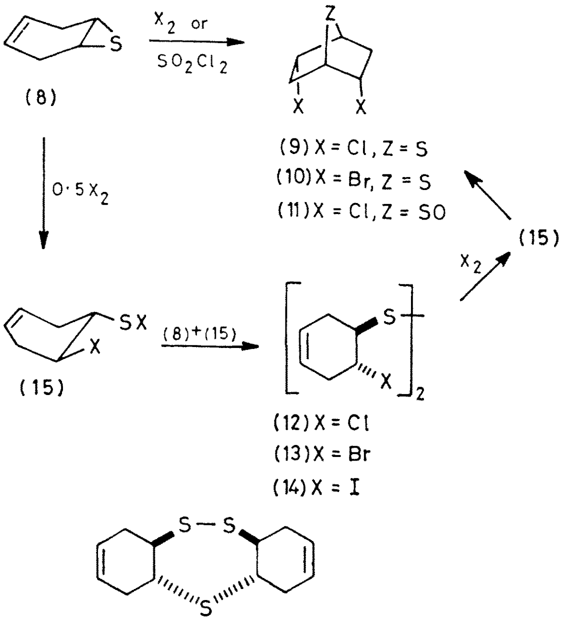


(2)

(6) X = Cl
(7) X = Br

To monitor the intermediates of these halogenolyses, the reactions of (**1**) with 1·1 mol of Br$_2$ in CDCl$_3$ or I$_2$ in CD$_2$Cl$_2$ were studied in the n.m.r. probe. At −30 °C, direct conversion into (**4**) or (**5**) occurred and no intermediates were detected even when the halogens were added in portions.

In contrast, reaction of (**8**)[6] at −40 °C in the n.m.r. probe with 1·1 mol of Br$_2$ in CDCl$_3$ gave (**10**), m.p. 60—62 °C [δ(CDCl$_3$) 3·63—3·83 (*H*–CS) and 4·30—4·72 (*H*–CBr); *m/e* 270, 272, and 274], *via* a clearly detectable unsaturated dibromide intermediate, which formed exclusively with 0·5 mol of Br$_2$ and could be isolated at room temperature. Treatment of (**8**) with 0·5 mol of I$_2$ in CFCl$_3$ at 0 °C furnished an unsaturated di-iodide, closely similar (spectra) to the above dibromide, but this remained unchanged on addition of an excess of iodine. These dihalides, C$_{12}$H$_{16}$Br$_2$S$_2$, *m/e* 382, 384, and 386 and C$_{12}$H$_{16}$I$_2$S$_2$, *m/e* 477·87815 (M^+), reacted with bromine to yield (**10**) and were assigned structures (**13**), b.p. 125—130 °C, 0·15 mmHg [δ (CDCl$_3$) 4·37—4·77 (*H*–CBr) and 5·47—5·73 (vinyl H); ν (CCl$_4$) 1661 cm^{-1}] and (**14**), b.p. 90—100 °C, 0·04 mmHg [δ (CDCl$_3$) 4·50—4·95 (*H*–CI); ν (CCl$_4$) 1658 cm^{-1}]. Furthermore, (**13**) condensed with sodium sulphide in tetrahydrofuran to give a trisulphide, tentatively formulated as (**16**)[11] [δ (CDCl$_3$) 3·1—3·8 (*H*–CS) and 5·7 (vinyl H); *m/e* 256 (M^+), 190 ($M-$H$_2$S$_2$), and 158 ($M-$H$_2$S$_3$)]. In preparative reactions, (**13**) and (**14**) were formed from (**8**) in 95 and 90% yield (of isolated material), respectively, and the conversions of (**13**) into (**10**) and (**8**) into (**10**) were quantitative.



(8)

(9) X = Cl, Z = S
(10) X = Br, Z = S
(11) X = Cl, Z = SO

(15)

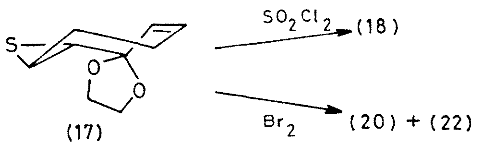
(12) X = Cl
(13) X = Br
(14) X = I

(16)

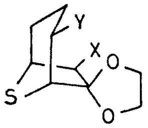
Reaction of (**8**) with an excess of Cl$_2$–CCl$_4$ gave a 2 : 5 (by n.m.r. spectroscopy) mixture of (**9**)[7] and (**11**), m.p. 110—115 °C [δ (CDCl$_3$) 3·59 (*H*–CSO), 4·04—4·50 (*H*–CCl), and 4·73—5·24 (*H*–CCl); *m/e* 198, 200, and 202], the latter being isolated (21%) by t.l.c., while chlorinolysis of (**8**) with SO$_2$Cl$_2$ (1 mol) in CH$_2$Cl$_2$ at 0 °C furnished exclusively (**9**) (94%). With 0·5 mol of SO$_2$Cl$_2$, (**8**) formed the disulphide (**12**) (97%), b.p. 95—100 °C, 0·03 mmHg (CDCl$_3$) 4·17—4·60 (*H*–CCl); ν (CCl$_4$) 1663 cm^{-1}].

Thus, halogenolysis of (**8**) proceeds by initial electrophilic ring opening of the thiiran, forming the sulphenyl halide (**15**), which condenses with unchanged substrate to yield a disulphide [(**12**), (**13**), or (**14**)], the latter reaction being faster. When an excess of Cl$_2$ or Br$_2$ is present, the disulphide is cleaved reforming (**15**), in which intramolecular addition of sulphenyl halide to the double bond occurs in the absence of substrate (**8**) [reaction of which with (**15**) must be faster] to form the bicyclic sulphides (**9**) and (**10**). Iodinolysis[8] of the disulphide (**14**) does not occur and (**11**) is produced from (**9**) by chlorine oxidation in presence of air.

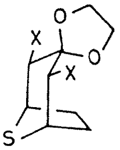
By analogy, electrophilic ring opening of the thiiran group of (**1**) also takes place first but the greater conformational flexibility of the eight-membered ring causes intramolecular condensation of sulphenyl halide with the double bond to be faster than disulphide formation.



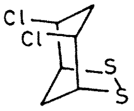
(17)



(18) X = Y = Cl
(19) X = Cl, Y = OH
(20) X = Y = Br



(21) X = Cl
(22) X = Br



(23)

Reaction of (**17**)[3] with 0·5 mol of SO_2Cl_2 furnished only starting material and (**18**), while, with 1·1 mol of SO_2Cl_2, (**18**)[9] was formed in 83% yield. Compound (**18**) underwent partial isomerisation and hydrolysis to (**19**)[9] and (**21**), m.p. 110—112 °C [δ ($CDCl_3$) 3·71 (*H*–CS), 4·01—4·47 (CH_2–O), and 4·54 (d, *J* 2 Hz, *H*–CCl), *m/e* 254, 256, and 258] when the mother liquor of crystallisation of (**18**) was chromatographed. Bromine treatment of (**17**) gave a 2 : 1 mixture of (**22**) and (**20**) (combined yield 94%) from which the former, m.p. 106—108 °C [δ ($CDCl_3$) 4·75 (d, *J* 2 Hz, *H*–CBr), *m/e* 342, 344, and 346], was isolated (35%) by crystallisation. Distillation (120—130 °C at 0·3 mmHg) of the mother liquor gave no further separation, the structural assignment of (**20**) being based on its n.m.r. similarity to (**18**).

The intermediacy of disulphides in the halogenolysis of (**8**) led us to investigate the possibility of creating an intramolecular disulphide bridge by an appropriate ring opening process. Reaction of (**8**) in CH_2Cl_2 (10^{-3} M) with SCl_2 at −50 °C gave a dichloro-disulphide [*m/e* 214, 216, 218 (M^+), 145, 147 ($M-SCl$), and 113, 115 ($M-S_2Cl$), λ_{max} (MeOH) 361 (ϵ 66) and 270 nm (33)], which possessed four distinct resonances (31·9, 34·7, 53·7, and 56·6 p.p.m.) in the noise-decoupled ^{13}C n.m.r. spectrum and showed complex ^1H n.m.r. absorption. These spectroscopic properties are compatible with structure (**23**)[10] and the formation of this compound represents a new method of preparing a cyclic disulphide (42% yield).

The above results demonstrate that reaction of unsaturated thiirans with electrophiles proceeds by initial ring opening of the episulphide group, providing a high-yield route to sulphides and, in certain cases, disulphides.

Satisfactory microanalytical data have been obtained for (**10**), (**12**), (**13**), (**21**), (**22**), and (**23**) and mass measurement for (**14**). Compounds (**12**)—(**14**) and (**16**) are depicted in only one diastereomeric form.[11]

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