

Preparation of Episulphides from Alkenes via Succinimide-*N*-sulphenyl Chloride or Phthalimide-*N*-sulphenyl Chloride Adducts

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Succinimide- and phthalimide-sulphenyl chlorides are formed in high yield from the corresponding disulphides by chlorinolysis at 50 °C. These imido-sulphenyl halides react in methylene chloride with cyclohexene, cyclopentene, cyclo-octene, styrene, methylenecyclohexane, and norbornene to form addition products which can subsequently be reduced with lithium aluminium hydride at -78 °C to form episulphides in good yield (49–97%). This new method compares very favourably with other literature routes.

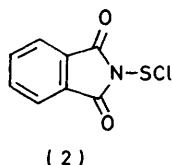
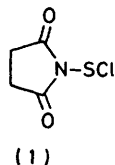
THE preparation of episulphides from alkenes has been extensively studied.^{1,2} The most common of the literature methods involves prior conversion of the alkene to the epoxide followed, in a subsequent step, by reaction with a sulphur transfer species such as thiocyanate,³ thioamides,^{3,4} triphenylphosphine sulphide,⁵ or carbon disulphide in the presence of a catalyst.⁶

Other useful methods include treatment of the adducts of alkenes and sulphur monochloride or sulphur dichloride with sodium sulphide⁷ or potassium *t*-butoxide,⁸ or by reaction of arenethiosulphenyl chloride adducts with either sodium sulphide or sodium amide at 80–90 °C.⁹ Direct episulphidation of alkenes by a photochemical reaction with carbonylsulphide¹⁰ or isothiocyanate¹¹ is also known; however, the yields are generally quite low.

As many of the above procedures seem to suffer from some synthetic limitation, a new method of preparation of episulphides is required. Here we report our results using succinimide-*N*-sulphenyl chloride and phthalimide-*N*-sulphenyl chloride adducts with alkenes as suitable episulphide precursors.

RESULTS AND DISCUSSION

Both succinimide-*N*-sulphenyl chloride (1) and phthalimide-*N*-sulphenyl chloride (2) were prepared in high yield from the corresponding disulphides by chlorinolysis in warm chloroform. However, we noticed that during the preparation of the disulphides the yield could be substantially increased over other literature methods¹² by using a modified procedure. For example, reaction of potassium succinimide in dichloromethane at 0 °C

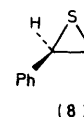
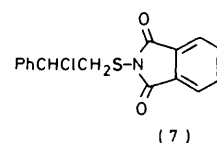
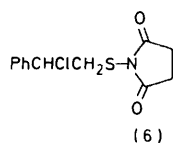
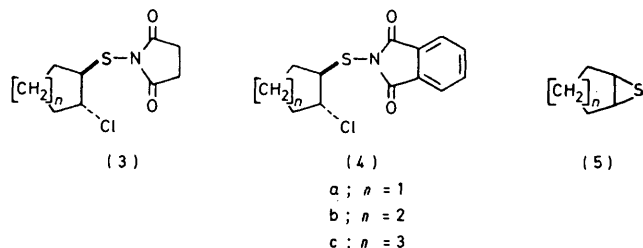


with sulphur monochloride gave a 79.3% yield of the disulphide. Similarly, *NN'*-dithiobis(phthalimide) could be isolated in 96.7% yield.

Although imidosulphenyl chlorides can be prepared by other routes,¹³ we found the above procedures to be the most convenient. The *N*-sulphenyl chlorides (1) and (2) are fairly stable and can be stored without

serious decomposition at 0 °C for a period of months. With the imidosulphenyl chlorides to hand, a number of cyclic alkene adducts were prepared in very high yield (73–100%). The assignment of *trans*-stereochemistry for these compounds, (3) and (4), is in accord with many literature precedents for sulphenyl halide-alkene adducts.¹⁴

The cyclopentene, cyclohexene, and cyclo-octene adducts, compounds (3) and (4), were all separately reduced with lithium aluminium hydride at -78 °C in THF, and after quenching with water afforded the corresponding episulphides (58–97%). Most impressive of these reactions was the formation of cyclopentene sulphide (5a) in 81% yield from the adduct (4a). This yield compares very favourably with other methods.¹

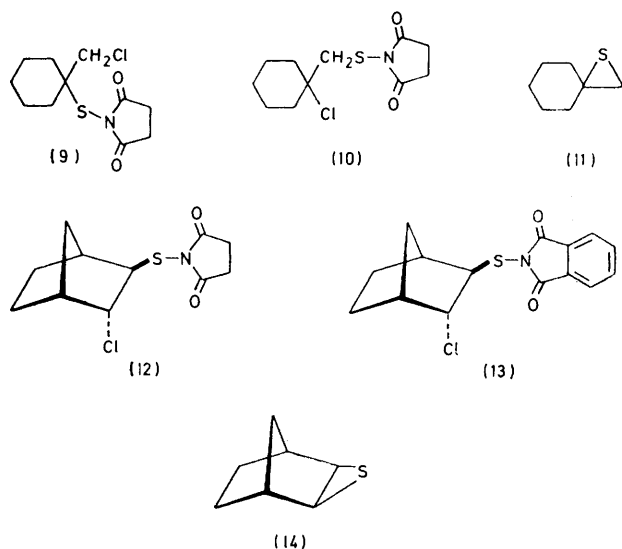


The imidosulphenyl chlorides (1) and (2) also readily react with styrene to form the corresponding adducts (6) and (7). The structure of these adducts followed from their ¹H n.m.r. spectra. For example, (6) shows the X part of an ABX spectrum centred at δ 5.08, corresponding to the methine proton adjacent to a phenyl and a chlorine group. Had the compound been the other possible regio-isomer, the methine proton would have been expected at significantly higher field. Similarly, (7) shows a low-field absorption centred at δ 5.18. Both (6) and (7) on treatment with lithium aluminium hydride at -78 °C produced styrene sulphide (8) in excellent yield (89 and 96%, respectively).

Reaction of methylenecyclohexane with succinimide-*N*-sulphenyl chloride (1) at room temperature leads to the formation of the adduct (9) in essentially quanti-

tative yield. The ^1H n.m.r. spectrum of (9) clearly shows the absorption due to the CH_2Cl group at δ 3.7. On warming in methanol, (9) rearranges to the other regio-isomer (10). This rearrangement can be followed in the ^1H n.m.r. spectrum, which shows a new signal appearing at δ 2.8 corresponding to the CH_2 group next to a sulphur substituent. Treatment of (9) with lithium aluminium hydride at -78°C , followed by aqueous work-up, affords the episulphide (11) in 48% yield. As compound (10) was not isolated in a pure state its conversion to the episulphide (11) was not investigated.

Finally, bicyclo[2.2.1]hept-2-ene (norbornene) also rapidly reacted with succinimide-*N*-sulphenyl chloride and phthalimide-*N*-sulphenyl chloride to give (12) and (13), respectively. The ^1H n.m.r. spectra are in full agreement with the assigned structures. Reduction of (12) and (13) furnishes in high yield the episulphide (14), the *exo* stereochemistry of which was assigned by direct spectral comparison with an authentic sample.



It is apparent, therefore, that imidosulphenyl chloride-alkene adducts are reasonable precursors for the preparation of a variety of episulphides.

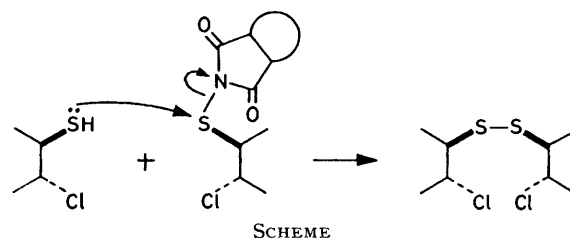
Concerning the mechanism for the formation of the episulphide, we propose that the lithium aluminium hydride first reduces the S-N bond to form a thiol intermediate, which rapidly reacts with excess of the hydride reagent to form a thiolate anion. On warming, this anion readily cyclises by nucleophilic displacement of a chloride ion.¹⁵

In an effort to develop a one-pot procedure, we found that even if the lithium aluminium hydride was added to a cold (-78°C) solution of the adducts, the initially formed thiol, in the absence of excess of hydride reagent, was sufficiently reactive to displace the imido-group from another molecule of adduct to form the disulphide as an undesirable side product (Scheme).¹⁶

Other methods for reducing the S-N bond such as

sodium borohydride or Zn-H^+ were studied, but were unsuccessful in producing episulphides.

The use of these imidosulphenyl chloride alkene adducts as precursors to other sulphur containing compounds is currently under investigation.



EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. ^1H N.m.r. spectra were obtained for solutions in CDCl_3 (SiMe_4 as internal standard) at 60 MHz. Thin layer and preparative layer chromatography were carried out on silica gel (Merck GF₂₅₄ Typ 60). Light petroleum refers to the fraction of b.p. $60-80^\circ\text{C}$. Solutions were dried over magnesium sulphate and solvents dried by standard techniques.

NN'-Dithiobis(succinimide).—A hot solution of succinimide (100 g) in absolute ethanol (1 l) was poured into an ice-cold solution of potassium hydroxide (58 g) in absolute ethanol (300 ml). The mixture was stirred and cooled to 0°C . Potassium succinimide crystallized from the mixture, as colourless crystals, and was collected by suction filtration. After washing with light petroleum the crystals were dried (110.3 g, 79.1%). A solution of sulphur monochloride (54 g) in dichloromethane (50 ml) was added over 5 min to a vigorously stirred suspension of the potassium succinimide (110.3 g) in dichloromethane (400 ml) at 0°C . After the initial exothermic reaction, the mixture was stirred for a further 5 min, filtered, and the filtrate evaporated *in vacuo* to leave a solid residue, which was washed three times with light petroleum and once with water. Crystallization from methanol gave colourless plates of *NN'*-dithiobis(succinimide) (83 g, 79.3%), m.p. $192-193^\circ\text{C}$; δ 2.83 (s, CH_2); *m/e* 260, 162, 134, 102, 99, and 55.

Succinimide-N-Sulphenyl Chloride.—Chlorine gas was passed for 8 h through a stirred solution of the *NN'*-dithiobis(succinimide) (53.7 g) in chloroform (250 ml) warmed to 50°C . Nitrogen gas was passed through the mixture to remove excess of chlorine, followed by evaporation *in vacuo* to give succinimide-*N*-sulphenyl chloride (1) (65.1 g, 93.3%) as yellow crystals, m.p. $65-67^\circ\text{C}$, δ 3.00 (s, CH_2).

NN'-Dithiobis(phthalimide).—By a similar method to that above a stirred suspension of potassium phthalimide (73.3 g) in methylene chloride (400 ml) at 0°C was added to a solution of sulphur monochloride (26 g) in dichloromethane (15 ml) during 5 min. Recrystallisation of the crude product from chloroform afforded *NN'*-dithiobis(phthalimide) (67.9 g, 96.7%) as large colourless needles, m.p. $229-230^\circ\text{C}$ (lit.,¹² 230°C); δ (CD_3COCD_3) 7.77 (m, aryl-H); *m/e* 356, 210, 178, 147, 130, and 104.

Phthalimide-N-Sulphenyl Chloride.—Chlorine gas was bubbled for 8 h through a stirred solution of *NN'*-dithiobis(phthalimide) (58.8 g) in chloroform (300 ml) maintained at $50-60^\circ\text{C}$. After work-up as above, this gave phthalimide-*N*-sulphenyl chloride (2) (69.1 g, 98%) as yellow crystals, m.p. $115-117^\circ\text{C}$; δ 7.75-8.2 (4 H, m).

General Procedure for the Preparation of Imidosulphenyl Chloride-Alkene Adducts and Their Reduction to Episulphides.—The imidosulphenyl chloride was dissolved in dry CH_2Cl_2 to form a yellow solution which was added dropwise at room temperature to the alkene dissolved in CH_2Cl_2 . The mixture was stirred until no yellow colour persisted. Removal of the solvent under reduced pressure gave the adduct, which was crystallised from the appropriate solvent. The adduct in dry THF was added dropwise to a stirred suspension of lithium aluminium hydride in THF at -78°C . After stirring for a further 10 min, the mixture was allowed to warm to room temperature and quenched with water. The episulphide was extracted with ether and after drying (MgSO_4) and removal of the solvent, distilled under reduced pressure to afford the pure episulphide.

Cyclopentene Sulphide.—(a) From *trans-N*-(2-chlorocyclopentylthio)succinimide. Cyclopentene (5 g, 0.0735 mol) in dichloromethane (25 ml) with succinimide-*N*-sulphenyl chloride (9.5 g, 0.057 mol) in dichloromethane (50 ml) gave *trans-N*-(2-chlorocyclopentylthio)succinimide (3a) (13.3 g, 99.2%) as an oil; δ 1.30—2.30 (6 H, m, 3 CH_2), 2.87 (4 H, s, 2 CH_2), 3.60—3.95 (1 H, m), and 4.13—4.43 (1 H, m); *m/e* 235, 233, 197, 134, 99, and 67 (Found: C, 46.2; H, 5.1; Cl, 15.2; N, 5.75; S, 13.9. $\text{C}_9\text{H}_{12}\text{ClNO}_2\text{S}$ requires C, 46.25; H, 5.2; Cl, 15.15; N, 6.0; S, 13.7%).

Ethanol (2.8 g) in THF (5 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (2 g) in THF (25 ml) at 0°C under nitrogen. After 15 min, the mixture was cooled to -78°C and *trans-N*-(2-chlorocyclopentylthio)succinimide (13.3 g, 0.057 mol) in THF (25 ml) was added dropwise to the stirred reducing agent. When addition was complete, the mixture was allowed to warm to room temperature and worked up to afford cyclopentene sulphide (5a) (3.3 g, 58%); δ 3.2 (2 H, br s) and 1.2—2.3 (6 H, m).

(b) From *trans-N*-(2-chlorocyclopentylthio)phthalimide. Phthalimide-*N*-sulphenyl chloride (5 g, 0.0234 mol) in dichloromethane (25 ml) with cyclopentene (1.7 g, 0.025 mol) gave *trans-N*-(2-chlorocyclopentylthio)phthalimide (4a) (5.3 g, 80.4%) as colourless plates (from methanol), m.p. 104—105 $^\circ\text{C}$; δ 1.00—2.30 (6 H, m, 3 CH_2), 3.13—3.50 (1 H, m), 3.87—4.10 (1 H, m), and 7.42 (4 H, m, aryl-H); *m/e* 283, 281, 245, 179, 147, and 91 (Found: C, 55.35; H, 4.3; Cl, 12.85; N, 4.9; S, 11.3. $\text{C}_{13}\text{H}_{12}\text{ClNO}_2\text{S}$ requires C, 55.4; H, 4.3; Cl, 12.6; N, 4.95; S, 11.4%).

trans-N-(2-Chlorocyclopentylthio)phthalimide (4.5 g, 0.016 mol) in THF (25 ml) was added dropwise to a stirred suspension of LiAlH_4 (1 g) in THF (25 ml) at -78°C and on work-up gave cyclopentene sulphide (5a) (1.3 g, 81.3%), identical by n.m.r. to the previous sample.

Cyclohexene Sulphide.—(a) From *trans-N*-(2-chlorocyclohexylthio)succinimide. Succinimide-*N*-sulphenyl chloride (6.5 g, 0.0393 mol) in dichloromethane (15 ml) with cyclohexene (5 g, 0.061 mol) in dichloromethane (25 ml) afforded on work-up *trans-N*-(2-chlorocyclohexylthio)succinimide (3b) (9.7 g, 99.79%) as a colourless gum; δ 1.20—2.20 (8 H, m, 4 CH_2), 2.83 (4 H, s, 2 CH_2), 3.20—3.57 (1 H, m), and 3.83—4.2 (1 H, m); *m/e* 249, 247, 211, 150, 148, 131, 99, and 81 (Found: C, 48.2; H, 5.55; Cl, 14.05; N, 5.65; S, 12.95. $\text{C}_{10}\text{H}_{14}\text{ClNO}_2\text{S}$ requires C, 48.5; H, 5.7; Cl, 14.3; N, 5.65; S, 12.95%).

trans-N-(2-Chlorocyclohexylthio)succinimide (9.7 g, 0.0392 mol) in THF (15 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (1.4 g) in

THF (25 ml) at -78°C under nitrogen, and after work-up gave cyclohexene sulphide (5b) (3.1 g, 69.4%); δ 3.1—3.3 (2 H, m), 1.85—2.5 (4 H, m), and 1.0—1.85 (4 H, m).

(b) From *trans-N*-(2-chlorocyclohexylthio)phthalimide. Cyclohexene (6 g, 0.073 mol) in dichloromethane (100 ml) with phthalimide-*N*-sulphenyl chloride (11 g, 0.052 mol) in dichloromethane (50 ml) afforded *trans-N*-(2-chlorocyclohexylthio)phthalimide (4b) (14.2 g, 93.3%) as colourless needles (from methanol), m.p. 138—140 $^\circ\text{C}$; δ 1.17—1.80 (8 H, m, 4 CH_2), 3.00—3.23 (1 H, m), 3.87—4.20 (1 H, m), and 7.67—8.00 (4 H, m, aryl-H); *m/e* 297, 295, 259, 179, 148, 105, 91, and 81 (Found: C, 56.85; H, 4.65; Cl, 11.8; N, 4.7; S, 10.55. $\text{C}_{14}\text{H}_{14}\text{ClNO}_2\text{S}$ requires C, 56.85; H, 4.75; Cl, 12.0; N, 4.75; S, 10.85%).

trans-N-(2-Chlorocyclohexylthio)phthalimide (7.00 g, 0.037 mol) in THF (50 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (1 g) in THF (25 ml) at -78°C under nitrogen. After work-up this gave cyclohexene sulphide (5b) (2.5 g, 92.5%), identical to the previous sample.

Cyclo-octene Sulphide.—(a) From *trans-N*-(2-chlorocyclo-octylthio)succinimide. Succinimide-*N*-sulphenyl chloride (6.6 g, 0.04 mol) in dichloromethane (25 ml) with cyclo-octene (4.5 g, 0.041 mol) in methylene chloride (50 ml) on work-up gave *trans-N*-(2-chlorocyclo-octylthio)succinimide (3c) (9.4 g, 85.3%), m.p. 83—85 $^\circ\text{C}$ (from ether); δ 1.17—2.27 (12 H, m, 6 CH_2), 2.77 (4 H, s, 2 CH_2), 3.57—3.83 (1 H, m), and 4.23—4.50 (1 H, m); *m/e* 277, 275, 260, 239, 211, 176, 141, 109, and 99 (Found: C, 52.45; H, 6.65; Cl, 12.7; N, 4.95; S, 11.55. $\text{C}_{12}\text{H}_{18}\text{ClNO}_2\text{S}$ requires C, 52.25; H, 6.6; Cl, 12.85; N, 5.1; S, 11.65%).

The *trans-N*-(2-chlorocyclo-octylthio)succinimide (9.4 g, 0.034 mol) in THF (25 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (1.1 g) in THF (10 ml) at -78°C . This after work-up gave cyclo-octene sulphide (5c) (4.7 g, 97.35%), b.p. 50 $^\circ\text{C}$ at 0.7 mmHg (lit.,¹⁷ 71 $^\circ\text{C}$ at 2 mmHg); δ 2.7—3.1 (2 H, m), 2.0—2.5 (2 H, m), and 1.1—1.8 (8 H, m).

(b) From *trans-N*-(2-chlorocyclo-octylthio)phthalimide. Phthalimide-*N*-sulphenyl chloride (5.5 g, 0.026 mol) in dichloromethane (50 ml) with cyclo-octene (3 g, 0.027 mol) in methylene chloride (20 ml) on work-up gave *trans-N*-(2-chlorocyclo-octylthio)phthalimide (4c) (8.3 g, 73.65%) as colourless crystals (from methanol), m.p. 87—88 $^\circ\text{C}$; δ 1.00—2.13 (12 H, m, 6 CH_2), 3.20—3.80 (1 H, m), 4.30—4.63 (1 H, m), and 7.67—8.00 (4 H, m, aryl-H); *m/e* 325, 323, 281, 259, 179, 147, 105, and 91 (Found: C, 59.5; H, 5.6; Cl, 11.0; N, 4.35; S, 10.0. $\text{C}_{16}\text{H}_{18}\text{ClNO}_2\text{S}$ requires C, 59.35; H, 5.6; Cl, 10.95; N, 4.35; S, 9.9%).

To a stirred suspension of lithium aluminium hydride (0.7 g) in THF (20 ml) at -78°C was added dropwise a solution of the *trans-N*-(2-chlorocyclo-octylthio)phthalimide (8.3 g, 0.0257 mol) in THF (20 ml). Work-up gave cyclo-octene sulphide (5c) (3.5 g, 91.91%), b.p. 50—52 $^\circ\text{C}$ at 0.65 mmHg, identical by n.m.r. to the previously prepared sample.

Styrene Sulphide.—(a) From *N*-(1-chloro-2-phenylethylthio)succinimide. Succinimide-*N*-sulphenyl chloride (8 g, 0.0483 mol) in dichloromethane (50 ml) with styrene (5.2 g, 0.05 mol) in dichloromethane (50 ml) on work-up gave *N*-(1-chloro-2-phenylethylthio)succinimide (6) (13 g, 99.8%) as colourless crystals (from carbon tetrachloride), m.p. 95—100 $^\circ\text{C}$; δ 2.47 (4 H, s, 2 CH_2), 3.37—3.70 (2 H, q, CH_2), 4.93—5.17 (1 H, q, methine), and 7.30 (5 H, s, aryl-H); *m/e* 271, 269, 233, 139, 104, 99, and 91 (Found: C, 54.0;

H, 4.5; Cl, 12.95; N, 5.15; S, 11.75. $C_{12}H_{12}ClNO_2S$ requires C, 53.5; H, 4.45; Cl, 13.15; N, 5.2; S, 11.85%.

N-(1-Chloro-2-phenylethylthio)succinimide (6 g, 0.0223 mol) in THF (50 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (0.9 g) in THF (50 ml) at $-78^\circ C$. On work-up this afforded styrene sulphide (8) (2.7 g, 89.1%), b.p. $60^\circ C$ at 0.45 mmHg (lit.,¹⁸ $25-28^\circ C$ at 0.01 mmHg); δ 2.48 (1 H, dd, *J* 6 and 1.5 Hz), 2.7 (1 H, dd, *J* 6 and 1.5 Hz), 3.75 (1 H, t, *J* 6 Hz, methine), and 7.15 (5 H, s, aryl-H); *m/e* 136, 120, 104, 99, and 76.

(b) From *N*-(1-chloro-2-phenylethylthio)phthalimide. Phthalimide-*N*-sulphenyl chloride (5.6 g, 0.026 mol) in dichloromethane (20 ml) with styrene (3.6 g, 0.035 mol) in dichloromethane (25 ml) on work-up gave *N*-(1-chloro-2-phenylethylthio)phthalimide (7) (8.2 g, 100%), m.p. $95-96^\circ C$; δ 3.33—296 °C; δ 3.33—3.5 (2 H, m, CH_2), 4.97—5.23 (1 H, m, methine), 7.00—7.47 (5 H, m, Ph), and 7.67 (4 H, broad s, aryl-H); *m/e* 319, 317, 281, 178, 147, and 104 (Found: C, 60.5; H, 3.75; Cl, 11.05; N, 4.35; S, 10.3. $C_{16}H_{12}ClNO_2S$ requires C, 60.45; H, 3.8; Cl, 11.15; N, 4.4; S, 10.1%).

N-(1-Chloro-2-phenylethylthio)phthalimide (8.3 g, 0.036 mol) in THF (50 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (1 g) in THF (25 ml) at $-78^\circ C$. Work-up gave styrene sulphide (8) (3.4 g, 96.2%), b.p. $62^\circ C$ at 0.5 mmHg.

Cyclohexanespirothiiran.— Succinimide-*N*-sulphenyl chloride (5.8 g, 0.032 mol) in dichloromethane (25 ml) with methylenecyclohexane (4.5 g, 0.047 mol) afforded [1-(*N*-succinimidothio)cyclohexyl]chloromethane (9) (8.3 g, 10%) as a mobile oil; δ 1.00—2.10 (10 H, m, 5 CH_2), 2.90 (4 H, s, 2 CH_2), and 3.70 (2 H, s, CH_2); *m/e* 263, 261, 225, 194, 162, 126, 95, and 81.

The above sulphenimide (9 g, 0.0344 mol) in THF (25 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (0.9 g) in THF (25 ml) at $-78^\circ C$. Work-up gave cyclohexanespirothiiran (11) (2.00 g, 48.83%), b.p. $30^\circ C$ at 0.6 mmHg (lit.,¹⁹ $61-63^\circ C$ at 13 mmHg); δ 1.00—2.00 (10 H, m, 5 CH_2) and 2.32 (2 H, s, CH_2); *m/e* 128, 95, 81, and 67.

exo-2,3-*Epithionorbornane*.—(a) From *endo*-3-chloro-*exo*-2-(*N*-succinimidothio)bicyclo[2.2.1]heptane. Succinimide-*N*-sulphenyl chloride (1.7 g, 0.0103 mol) in dichloromethane (10 ml) with norbornene (0.99 g, 0.0105 mol) in dichloromethane (15 ml) afforded *endo*-3-chloro-*exo*-2-(*N*-succinimidothio)bicyclo[2.2.1]heptane (12) (2.7 g, 100%) as a colourless gum, δ 1.2—2.7 (8 H, m), 2.95 (4 H, s), 3.2—3.4 (1 H, m), 4.23 (1 H, t, *J* 3 Hz).

endo-3-chloro-*exo*-2-(*N*-succinimidothio)bicyclo[2.2.1]heptane (2.5 g, 0.01 mol) was dissolved in THF (10 ml) and the solution was added dropwise to a stirred suspension of lithium aluminium hydride (0.4 g) in THF (25 ml) at $-78^\circ C$. Work-up gave *exo*-2,3-*epithionorbornane* (14) (1 g, 79.4%), b.p. $28^\circ C$ at 0.1 mmHg (lit.,²⁰ $30-31^\circ C$ at 5 mmHg); δ 0.62 (H, d, *J* 10 Hz, *anti*-7-H), 1.25 (H, d, *J* 10 Hz, *syn*-7-H), 1.27—1.83 (4 H, m, 2 CH_2), 2.43 (2 H, br s), and 2.73 (2 H, s); *m/e* 126 and 94.

(b) From *endo*-3-chloro-*exo*-2-(*N*-phthalimidothio)bicyclo[2.2.1]heptane. Phthalimide-*N*-sulphenyl chloride (3 g, 0.0141 mol) in dichloromethane (10 ml) with norbornene (1.6 g, 0.017 mol) in dichloromethane (25 ml) afforded *endo*-3-chloro-*exo*-2-(*N*-phthalimidothio)bicyclo[2.2.1]heptane (13) (4.3 g, 100%) as colourless crystals (from methanol), m.p. $113^\circ C$; δ 1.2—2.7 (8 H, m), 3.14—3.3 (1 H, m), 4.23 (1 H, t, *J* 3 Hz), and 7.6—8.2 (4 H, m); *m/e* 309, 307, 271, 205, 179, and 160 (Found: C, 58.45; H, 4.5; Cl, 11.35; N, 4.5; S, 10.35. $C_{15}H_{14}ClNO_2S$ requires C, 58.55; H, 4.6; Cl, 11.5; N, 4.55; S, 10.4%).

Ethanol (0.8 g) in THF (4 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (0.9 g) in THF (25 ml) at $0^\circ C$ under nitrogen. The mixture was subsequently cooled to $-78^\circ C$, and *endo*-3-chloro-*exo*-2-(*N*-phthalimidothio)bicyclo[2.2.1]heptane (4.2 g, 0.0137 mol) in THF (10 ml) was added dropwise to the stirred reducing agent over 1.5 h. Work-up gave *exo*-2,3-*epithionorbornane* (14) (1 g, 57.94%).

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