

VIC-IODOTHIOCYANATES AND IODOISOTHIOCYANATES. PART 6. THE SYNTHESIS OF THIIRANS

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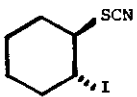
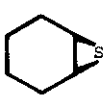
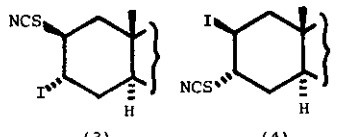
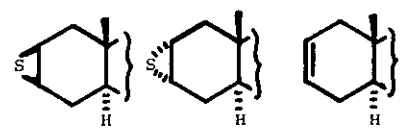
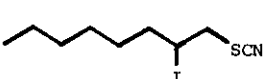
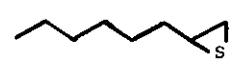
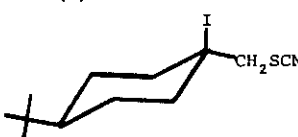
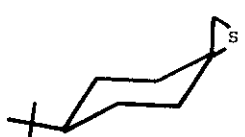
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Abstract - Treatment of the vic-iodothiocyanates of either cyclic or acyclic alkenes with lithium triethylborohydride ('Super Hydride') gives thiiirans in high yields. The structure of the product from r-1-iodo-1-thiocyanatomethyl-c-4-t-butylcyclohexane has been confirmed by an independent synthesis.

Recently, we¹ confirmed Hinshaw's² finding that treatment of the trans-iodothiocyanates of cyclic alkenes with methanolic potassium hydroxide at room temperature afforded thiiirans (episulfides) in moderate yields. However, the procedure was unsuitable for acyclic alkenes which gave mixtures of high boiling malodorous products rather than synthetically useful thiiirans, a fact which can be attributed to the ease with which acyclic vic-iodothiocyanates undergo elimination. We also showed¹ that use of the weaker nucleophile but stronger base potassium t-butoxide ultimately gives a quantitative yield of the thiiiran (2) from the iodothiocyanate (1) in a slow reaction. In contrast, use of n-butyl-lithium results mainly in metal-halogen exchange and subsequent elimination when the steroidal derivative (3) is treated with this reagent.³ Thus, the choice of a suitable nucleophile is crucial to the synthetic utility of this method for the preparation of thiiirans.

We have now found that lithium triethylborohydride ('Super Hydride')⁴ not only provides a suitable base for the formation of thiiirans from the trans-iodothiocyanates of cyclic alkenes but also serves as an effective reagent for the stereospecific synthesis of mono- and di-substituted thiiirans from acyclic vic-iodothiocyanates. Some results are presented in the Table. The thiiirans were identified by comparison of their ¹H n.m.r. spectra with reported data [(2), ¹(5), ¹(6), ¹(9), ⁵], or in the case of (11) with that of a sample synthesized by an independent route. Confirmatory evidence was provided by mass spectral analysis; in particular the spectrum of 2-hexylthiiiran (9) and of t-6-t-butyl-1-thiaspiro[2.5]octane (11) showed the molecular ion at m/z 144 and 184 respectively. The isolation of 5 α -androst-2-ene (7) from the reaction of (3) and (4) is attributed to selective desulfurisation of the 2 α ,3 α -thiiiran (6) (cf. the relative ratio

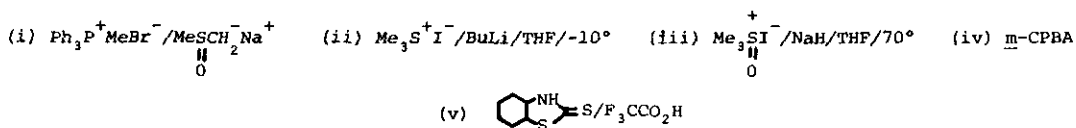
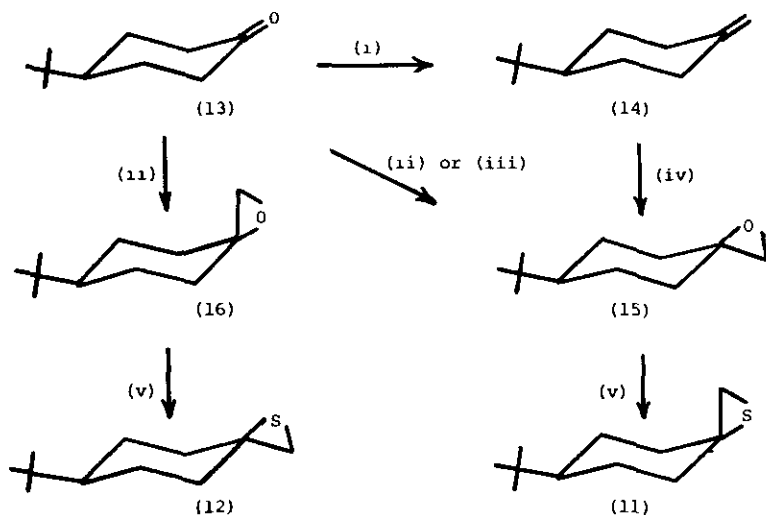
of products with that of reactants) during isolation since the alkene was not detected (t.l.c. analysis) prior to work-up.

<u>vic</u> -Iodothiocyanate ^{a,b}	Thiiran	Yield(%) ^c
 (1)	 (2)	93
 (3) (4)	 (5) (6) (7)	91
(1:4)	(1:3:1)	
 (8)	 (9)	87 ^d
 (10)	 (11)	100

^aThe molar ratio of vic-iodothiocyanate: LiEt₃BH was 1:1.2. ^bReactions were carried out in the dark under dry N₂, using dried solvents. ^cYields after work-up; ratios from ¹H n.m.r. analysis. ^dUse of LiAlH₄ (2 equiv.) as the reagent gave a mixture of dioctyl sulfides, dioctyl disulfides, and starting material. Use of DABCO as the reagent gave (E)-1-thiocyanato-oct-1-ene (46%) and starting material.

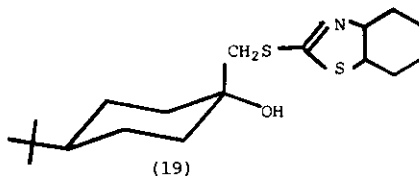
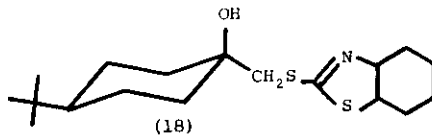
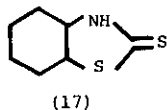
The stereochemistry of the thiiran (11) which was confirmed by independent syntheses of the cis- and trans-stereoisomers (12) and (11), represents clean inversion at the quaternary carbon during the intramolecular displacement of iodide. The synthetic approaches to compounds (11) and (12) are outlined in Scheme 1. The cis- and trans-oxirans (15) and (16) of well-defined

Scheme 1

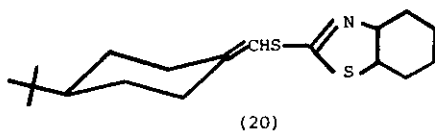


stereochemistry, were prepared by the action of sulfur ylides⁶ on 4-t-butylcyclohexanone (13) or by epoxidation⁷ of 1-methylene-4-t-butylcyclohexane (14) with \underline{m} -chloroperbenzoic acid following literature procedures. In only one case, *viz.* step (iii) (Scheme 1), was a single oxiran obtained, this being the *cis*-isomer (15) in accord with the known stereochemistry of the reaction.⁶ In the case of step (ii) (Scheme 1) it was found necessary to deoxygenate both the suspension of the trimethylsulfonium methylide and the solution of the ketone (13) with a stream of dry inert gas and to keep the temperature below 0° in order to avoid decomposition of the ylide.⁶ The ratio of (15): (16) obtained, *viz.* 57:43, differed from that (17:83) reported,⁶ presumably reflecting an accumulation of the thermodynamically favoured *cis*-oxiran (15).⁸

In preliminary studies a mixture (7:2) of the oxirans (15) and (16) was treated with equimolar amounts of the thiation reagent *cis*-3a,4,5,6,7,7a-hexahydrobenzothiazolidine-2-thione (17)⁹ and trifluoroacetic acid in dideuteriodichloromethane; the latter solvent was used to enable the course of the reaction to be monitored by ¹H n.m.r. analysis. After 5 minutes an 86% yield of



a mixture (3:1) of the compounds (18) and (19) was isolated. On the other hand, prolonged (72 h) reaction of a mixture (1.3:1) of (15) and (16) using a catalytic amount (4 mol %) of trifluoroacetic acid gave an inseparable mixture (1.4:1) of t-6-*t*-butyl-1-thiaspiro[2.5]octane (11) and c-6-*t*-butyl-1-thiaspiro[2.5]octane (12) which were identified from ^1H n.m.r. and mass spectral data. Signals at δ 2.29 and 2.44 in the ^1H n.m.r. spectra of (11) and (12) respectively, were comparable to those of the exocyclic methylene protons of similar thirans,⁵ that of (11) appearing as two sharp lines with separation 1.6 Hz. Since the methylene protons are not inherently diastereotopic the latter splitting could arise from the fact that each proton undergoes one long-range W coupling to an axial proton on either C4 or C8. Thus the methylene protons are symmetry related and appear as a doublet in the ^1H n.m.r. Analogous coupling is not possible

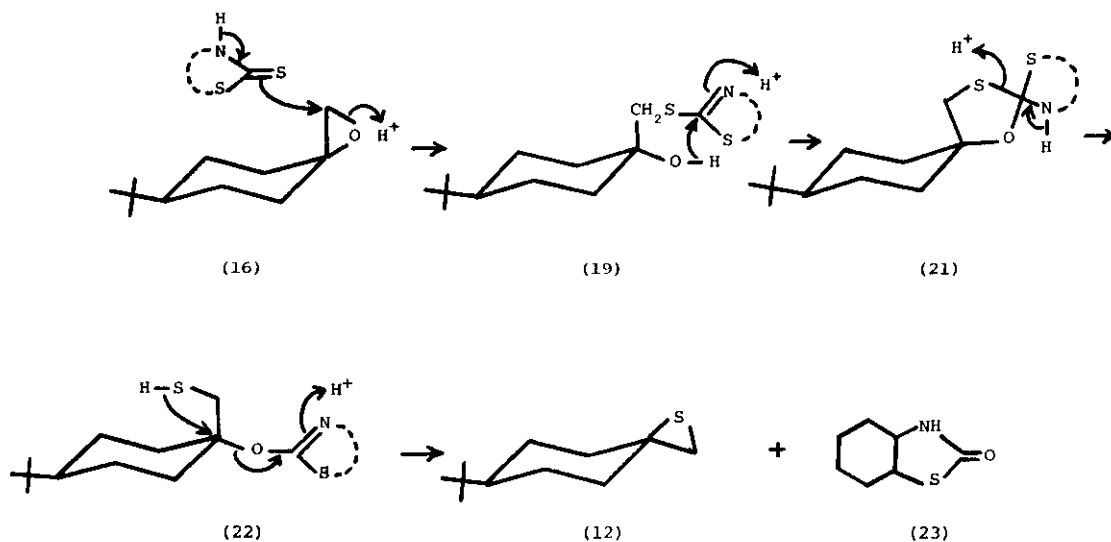


in the isomer (12). The appearance and subsequent disappearance of signals centred at δ 3.16 and 3.31 in the ^1H n.m.r. spectrum during the reaction suggested the formation and destruction of the intermediates (18) and (19). In order to isolate and characterise these intermediates a mixture (1.3:1) of the oxirans (15) and (16) was treated with the thiazolidine-2-thione (17) in dichloromethane in the presence of 1 mol equivalent of trifluoroacetic acid at room temperature for 15 min. Separation of the products by p.l.c. gave low yields of (18) and (19), the latter being contaminated by the thioenol ether (20). In the ^1H n.m.r. spectrum of (18) in

deuteriochloroform the CH_2S protons appeared to be nearly equivalent, resonating as a broad singlet at δ 3.15. In dideuteriodichloromethane however, these diastereotopic protons resonated separately at δ 2.97 and 3.29. The ^1H n.m.r. spectrum of (19) in deuteriochloroform indicated that the thioether (20) was in fact the impurity since two *t*-butyl resonances (ca. 1:1 intensity ratio) were present at δ 0.85 and 0.88 while a broad singlet at δ 5.75 corresponded with that of a vinyl proton of a thioenol ether.¹⁰ This assignment was supported by the presence of a weak $\text{C}=\text{C}$ absorption at 1660 cm^{-1} in the i.r. spectrum. The thioenol ether (20) presumably arises by acid-catalysed loss of water from the thio-alcohol (19) since it was not detected by ^1H n.m.r. analysis prior to work-up.

When treated separately with trifluoroacetic acid (4 mol %) in dideuteriodichloromethane at 35° for 14 h, the intermediate (19) gave a quantitative yield of the cis-thiiran (12) and the intermediate (18) gave a quantitative yield of the trans-thiiran (11) [e.g. Scheme 2 for (16)→(12)]. Monitoring of the reactions by ^1H n.m.r. analysis showed the appearance and disappearance of

Scheme 2



signals assigned to the intermediates (19), (21), and (22) for the conversion of (16) into (12), and of the corresponding intermediates for the conversion of (15) into (11). An intermediate analogous to (19) has been trapped by Meyers and Ford⁵ as its trimethylsilyl ether derivative

during the synthesis of thirans from carbonyl compounds using alkylthio-oxazolines as methylenethio-transfer reagents (see also ref. 11). In the present case accumulation of (18) and (19) at the expense of the starting oxirans occurred rapidly [the cis-oxiran (15) opening faster] especially when 1 mol equiv. of trifluoroacetic acid was used whereupon they became the predominant components of the reaction mixtures. However, accumulation of the thirans at the expense of the intermediates (18) or (19) was a slower process. These observations are similar to those of Meyers and Ford⁵ and are in accord with the ability of sulfur to act as a leaving group in the thiol-forming step and as a nucleophile in the ring closure to give the thiran [e.g. (22)+(12)].

Experimental

General experimental details are given in ref.12. Reactions involving air and moisture-sensitive reagents were carried out under an inert atmosphere in an oven-dried 3 necked flask equipped with a magnetic stirrer bar, gas inlet and bubbler, and a septum-capped inlet. Solvents and solutions were added with a nitrogen-flushed syringe.

Reactions of vic-Iodothiocyanates with Lithium Triethylborohydride.-

Lithium triethylborohydride (1 mol l⁻¹ in tetrahydrofuran) (0.13 - 0.65 ml) was added dropwise over 2 min to a stirred solution of the vic-iodothiocyanate (0.10 - 0.49 mmol) in dry ether (4 - 10 ml). The mixture was stirred in the dark under nitrogen at room temperature for 2 h; the progress of the reaction was followed by t.l.c. The mixture was diluted with ether, washed with water and brine, and the solvent was removed from the dried solution to give the product.

trans-1-Iodo-2-thiocyanatocyclohexane (1)¹² (0.13 g, 0.49 mmol) gave 7-thiabicyclo [4.1.0]heptane (2) (52 mg, 93%) (correct ¹H n.m.r. spectrum¹).

2-Iodo-1-thiocyanatooctane (8) (0.12 g, 0.39 mmol) gave 2-hexylthiiran (9) (49 mg, 87%) (correct ¹H n.m.r. spectrum⁵), m/z 144 (M⁺), and starting material (trace). A similar reaction in hexane gave a mixture (6:1) of (9) and starting material (45 mg, 82%).

trans-1-Iodo-1-thiocyanatomethyl-c-4-t-butylcyclohexane (10) (56 mg, 0.17 mmol) gave trans-6-t-butyl-1-thiaspiro[2.5]octane (11) as an oil (31 mg, 100%), ν_{max} 1070, 910, and 615 cm⁻¹, ¹H n.m.r. δ 0.87 (s, CMe₃), 1.00 - 2.22 (overlapping m, 4-H₂, 5-H₂, 7-H₂, 8-H₂, and 6-H), and 2.29 (2 lines, separation 1.6 Hz, 2-H₂), m/z 184 (M⁺), and 152 (M⁺-S).

A mixture (1:4) of 3 α -iodo-2 β -thiocyanato-5 α -androstane (3) and 2 β -iodo-3 α -thiocyanato-5 α -androstane (4)¹² (44 mg, 0.10 mmol) gave a mixture (1:3:1) of 2 β ,3 β -epithio-5 α -androstane (5) and 2 α ,3 α -epithio-5 α -androstane (6) (26.4 mg, 91%) (correct ¹H n.m.r. spectra⁹), and 5 α -androst-2-ene (7).

cis- and trans-6-t-Butyl-1-oxaspiro[2.5]octane (15) and (16).-

(a) Using trimethylsulfoxonium methylide. Trimethylsulfoxonium iodide (0.40 g, 1.82 mmol) was treated with sodium hydride (45 mg, 1.88 mmol) in tetrahydrofuran (15 ml) at 70 - 75° under nitrogen for 3 h, a solution of 4-t-butylcyclohexanone (13) (0.25 g, 1.62 mmol) in tetrahydrofuran (2 ml) was added, and the mixture was stirred at 70° for a further 3 h. Most of the solvent was removed in vacuo and the mixture was extracted with pentane. The extract was washed with water and brine, dried, and the solvent was removed to give a yellow oil (0.25 g) which was chromatographed on silica and eluted with hexane - ether (4:1) to give c-6-t-butyl-1-oxaspiro[2.5]octane (15) (0.20 g, 72%) as an oil (pure by ¹H n.m.r. analysis⁷).

(b) Using trimethylsulfonium methylide. A cooled (-10°) and stirred suspension of trimethylsulfonium iodide (0.86 g, 4.22 mmol) in dry tetrahydrofuran (30 ml) was deoxygenated with a stream of dry argon and treated dropwise with n-butyllithium (3.0 ml, 1.29 mmol ml⁻¹ in hexane) over ca. 2 min. The mixture was stirred at -10° for 4 min and then treated with a cooled, deoxygenated solution of 4-t-butylcyclohexanone (0.5 g, 3.25 mmol) in tetrahydrofuran (10 ml) over ca. 2 min. The mixture was stirred at -10° for a further 30 min and at room temperature for 1 h and then worked up to give a yellow oil (0.54 g) which was chromatographed on silica. Elution with hexane - ether (4:1) yielded a mixture (1.3:1) (0.42 g, 77%) of c-6-t-butyl-1-oxaspiro[2.5]octane (15) and t-6-t-butyl-1-oxaspiro[2.5]octane (16) (correct ¹H n.m.r. data⁷).

(c) Using m-chloroperbenzoic acid. A solution of 1-methylene-4-t-butylcyclohexane (14) (0.46 g, 3.05 mmol) in dichloromethane (30 ml) was treated with m-chloroperbenzoic acid (0.74 g, 3.66 mmol) at 0 - 3° for 5 h. The cold solution was filtered, and the filtrate was washed successively with aqueous sodium hydrogensulfite, saturated aqueous sodium hydrogencarbonate, and water. Removal of the solvent from the dried solution yielded a mixture (7:2) (0.46 g, 91%) of c-6-t-butyl-1-oxaspiro[2.5]octane (15) and t-6-t-butyl-1-oxaspiro[2.5]octane (16) (correct ¹H n.m.r. data⁷).

Reactions of cis- and trans-6-t-butyl-1-oxaspiro[2.5]octane (15) and (16) with cis-3a,4,5,6,7,7a-Hexahydrobenzothiazolidine-2-thione (17).-

(a) A mixture (7:2) (29 mg, 0.17 mmol) of the oxirans (15) and (16) in dideuteriodichloromethane (0.3 ml) was treated with the thiazolidine-2-thione (17) (30 mg, 0.17 mmol) and the solution was transferred to an n.m.r. tube. The ¹H n.m.r. spectrum which was recorded after 5 min at 35° indicated that no reaction had occurred. Trifluoroacetic acid (13 μl, 0.17 mmol) was added and the ¹H n.m.r. spectrum was recorded after a further 5 min at 35°; δ (CD₂Cl₂ - F₃CCO₂H) 0.87 (s, CMe₃), 3.40 (br s), 3.50 (br s), 3.74 - 4.62 (br m), and 5.30 (br s). The

mixture was extracted with dichloromethane, washed with water, saturated aqueous sodium hydrogen-carbonate, and brine, and the solvent was then removed from the dried solution to yield a mixture (ca. 3:1) (50 mg, 86%) of (18) and (19) (correct ^1H n.m.r. spectra; see below). The thirans (11) and (12) (ca. 3:1, see below) were also present in trace amounts.

(b) A mixture (1.3:1) (29 mg, 0.17 mmol) of the oxirans (15) and (16) in dideuteriodichloromethane (0.3 ml), was treated with the thiazolidine-2-thione (17) (30 mg, 0.17 mmol) and trifluoroacetic acid (0.5 μl , 0.0065 mmol, 4 mol%) as above. The accumulation of the thirans (11) and (12) and the disappearance of (15), (16), (18), and (19), together with the appearance of signals at δ 3.50 - 4.17 [(m, CHS and CHN of (23)), and 6.57 [br s, NH of (23)], was monitored at 24 h intervals by ^1H n.m.r. analysis during which time the solution was allowed to stand at room temperature. Only the thirans (11) and (12) (ca. 1.5:1, and the thiazolidinone (23) remained after 48 h. P.l.c. (hexane - ether, 4:1) of the solution after 72 h yielded a mixture (1:1.4) (15 mg, 48%) of c-6-t-butyl-1-thiaspiro[2.5]octane (12) and t-6-t-butyl-1-thiaspiro[2.5]octane (11), ^1H n.m.r. δ 0.87 [s, CMe_3 of (11)], 0.91 [s, CMe_3 of (12)] 1.00 - 2.22 (overlapping m, CH_2 and CH), 2.29 [2 lines, separation 1.6 Hz, 2- H_2 of (12)], and 2.44 [s, 2- H_2 of (11)]. The mass spectrum of the mixture was almost identical with that of pure (11).

(c) A solution of the pure oxiran (15) (29 mg, 0.17 mmol) in dideuteriodichloromethane (0.3 ml) was treated with the thiazolidine-2-thione (17) (30 mg, 0.17 mmol) and trifluoroacetic acid (0.5 μl , 0.0065 mmol, 4 mol%) as above. The accumulation of (18) at the expense of (15) was monitored by ^1H n.m.r. analysis while the temperature of the solution was maintained at 35°. After 80 min the ratio of (16) to (18) was ca. 1:2, and the thiran (11) had begun to appear. After a further 48 h at room temperature, only the thiran (11) and the co-product thiazolidinone (23) remained.

cis- and trans-2-[(r-1-Hydroxy-4-t-butylcyclohexylmethyl)thio]-cis-3a,4,5,6,7,7a-hexahydrobenzothiazole (18) and (19).-

A solution of a mixture (1.3:1) (0.20 g, 1.17 mmol) of the oxirans (15) and (16) in dichloromethane (2 ml) was treated with the thiazolidine-2-thione (17) (0.21 g, 1.23 mmol) and trifluoroacetic acid (90 μl , 1.17 mmol) and the mixture was shaken to ensure thorough mixing and then stood at room temperature for 5 min. The mixture was diluted with dichloromethane, washed with water, aqueous saturated sodium hydrogen carbonate, and brine, and solvent was removed from the dried solution to give an oil (0.42 g), comprised (^1H n.m.r. analysis) of (18) and (19), together with unreacted thiazolidine-2-thione (17), and the oxirans in lesser amounts. P.l.c. (hexane - ether, 1:1) of a portion (0.39 g) yielded (i) 2-[(r-1-hydroxy-c-4-t-butyl-cyclohexylmethyl)thio]-cis-3a,4,5,6,7,7a-hexahydrobenzothiazole (18) (39 mg, 10%) which

crystallised from hexane as colourless plates, m.p. 92 - 94° (Found: C, 63.6; H, 9.7; N, 4.1. $C_{18}H_{31}NOS_2$ requires C, 63.3; H, 9.2; N, 4.1%), ν_{max} . ($CHCl_3$) 3240 (OH), and 1540 cm^{-1} (C=N), 1H n.m.r. δ 0.87 (s, CMe_3), 3.14 (s, CH_2S), 3.59 - 4.29 (overlapping m, CHN and CHS), and 4.63 (br s, exchanged by D_2O , OH), 1H n.m.r. δ (CD_2Cl_2) 0.87 (s, CMe_3), 2.97 and 3.29 (2d, J_{gem} 14 Hz, CH_2H_S), and 3.47 - 4.17 overlapping m, CHN, CHS, and OH), m/z 341 ($M^{+\cdot}$), 326 ($M^{+\cdot}-CH_3^{\cdot}$), 323 ($M^{+\cdot}-H_2O$), 308 ($M^{+\cdot}-H_2O-CH_3^{\cdot}$), and 187 ($C_8H_{13}NS_2^{+\cdot}$, 100%); and (ii) a mixture (ca. 1:1) (37 mg) of 2-[(r-1-hydroxy-t-4-t-butylcyclohexylmethyl)thio]-cis-3a,4,5,6,7,7a-hexahydrobenzothiazole (19) and 2-[(4-t-butylcyclohexylmethylene)thio]-cis-3a,4,5,6,7,7a-hexahydrobenzothiazole (20), ν_{max} . ($CHCl_3$) 3200 (OH), 1660 (C=C), and 1540 cm^{-1} (C=N), 1H n.m.r. δ 0.85 [s, CMe_3 of (20)], 0.88 [s, CMe_3 of (19)], 3.29 [s, CH_2S of (19)], 3.67 - 4.24 [overlapping m, CHN and CHS of (19) and (20)], 4.00 [br s, OH of (19)], and 5.75 [br s, CHS of (20)], m/z 341 ($M^{+\cdot}$), 326 ($M^{+\cdot}-CH_3^{\cdot}$), 323 ($M^{+\cdot}-H_2O$), 308 ($M^{+\cdot}-H_2O-CH_3^{\cdot}$), and 187 ($C_8H_{13}NS_2^{+\cdot}$, 100%).

Reactions of Compounds (18) and (19) with Trifluoroacetic Acid.-

(i) Trifluoroacetic acid (0.2 μ l, 0.0026 mmol, 10 mol %) was added to a solution of (18) (9 mg, 0.026 mmol) in deuteriodichloromethane (0.3 ml) and the mixture was allowed to stand at 35° for 14 h. After this time the 1H n.m.r. spectrum showed quantitative conversion to the trans-thiiran (11) and the co-product thiazolidinone (23).

(ii) Trifluoroacetic acid (0.1 μ l, 0.0013 mmol, 5 mol %) was added to a solution of (18) (9 mg, 0.026 mmol) in deuteriochloroform. The 1H n.m.r. spectrum was recorded after 5 min at 35°; a broad singlet δ 3.40 [CH_2S] equal in intensity to the singlet at δ 3.15 [CH_2S of (18)] was present. After 22 h at room temperature the peak of δ 3.40 had almost disappeared and a new peak at δ 3.25 [s, CH_2S] twice the intensity of the singlet at δ 3.15, had appeared. After a further 24 h at 35° only peaks due to the thiiran (12) and co-product thiazolidinone (23) were apparent.

(iii) A solution of a mixture (ca. 1:1) (14 mg) of (19) and (20) in dideuteriodichloromethane (0.3 ml) was treated with trifluoroacetic acid (0.2 μ l) and the solution was allowed to stand at 35° for 25 min. The 1H n.m.r. spectrum showed a weak signal at δ 3.50 [br s, CH_2S of (21)]. After 14 h at 35°, quantitative conversion of (19) to the cis-thiiran (12) and co-product thiazolidinone (23) had occurred. Peaks due to the thioenol ether (20) were still present, however, and persisted even after a further 48 h at 35°, without diminishing in intensity.

Reaction of 2-Iodo-1-thiocyanatooctane (8) with Lithium Aluminium Hydride.-

Lithium aluminium hydride solution in ether (1.55 ml, 0.11 mol⁻¹, 0.17 mmol) was added dropwise with stirring to a solution of 2-iodo-1-thiocyanatooctane (0.10 g, 0.34 mmol) in ether (4 ml), and the solution was stirred for 1 h. Work-up gave an oil (22 mg); p.l.c. (hexane - chloroform, 3:1) yielded (i) a mixture of dioctyl sulfide and dioctyl disulfides, ν_{\max} 1130cm⁻¹ (C-S), ¹H n.m.r. δ 0.56 - 2.16 (CH₃, CH₂), 2.56 - 4.54 (CHS and CH₂S), m/z 258 (M⁺); and (ii) starting material.

Reaction of 2-Iodo-1-thiocyanatooctane (8) with DABCO.-

A solution of 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.13 g, 1.15 mmol) in benzene (6 ml) was added to a solution of 2-iodo-1-thiocyanatooctane (0.28 g, 0.96 mmol) in benzene (2 ml) and the mixture left to stand at room temperature for 1 week. The mixture was extracted with ether, washed with 5% aqueous hydrochloric acid, water, saturated aqueous sodium hydrogencarbonate, brine, and dried. Removal of solvent gave an oil (0.19 g), p.l.c. of a portion (0.17 g) of which yielded (i) (E)-1-thiocyanato-oct-1-ene (69 mg, 46%) as an oil, b.p. (Kugelrohr) 55° at 0.55 mmHg (Found: C, 63.8; H, 8.8; N, 8.5. C₉H₁₅NS requires C, 63.9; H, 8.9; N, 8.3%). ν_{\max} 2140 (SCN), 1615 cm⁻¹ (C=C); ¹H n.m.r. δ 0.92 (t, CH₃) 1.33 (m, CH₂) 2.19 (dxt, 3-CH₂), 5.66 - 6.45 (m, 2-CH and CHSCN), m/z 169 (M⁺); and (ii) starting material (77 mg, 29%).

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