Regioselective Synthesis of Hydroxy Sulphides *via* Trifluoroacetoxysulphenylation of Derivatives of Allylic Alcohols

Zakaria K. M. Abd El Samii, Mohamed I. Al Ashmawy, and John M. Mellor *
Department of Chemistry, The University, Southampton, SO9 5NH

Reaction of manganese(III) acetate with diphenyl disulphide in dichloromethane–trifluoroacetic acid in the presence of allylic esters gives trifluoroacetoxy sulphides, which on hydrolysis readily afford vicinal hydroxy sulphides. With acetate esters, neighbouring group participation by the acetate functionality controls the reaction course. Thus regiospecific addition to allyl acetate affords after hydrolysis only 3-phenylthiopropane-1,2-diol. In contrast, with trifluoroacetate esters the inductive effects of the trifluoroacetate functionality lead to a different regiocontrol. Thus addition of diphenyl disulphide to allyl trifluoroacetate gives after hydrolysis only 2-phenylthiopropane-1,3-diol. The regio- and stereochemistry of addition to a variety of other allylic (and homoallylic) esters is described and the extension of this type of regiocontrol is discussed.

In the development of new methods for the functionalisation of alkenes there is the need to control both regiochemistry and stereochemistry in addition reactions. In those additions leading to the vicinal addition of a sulphur substituent and an oxygen substituent to an alkene, considerable control has been developed. Thus Trost *et al.*[1] have used dimethyl(methylthio)-sulphonium tetrafluoroborate as the electrophile and have developed regioselective routes to β-hydroxy sulphides. Earlier papers describe the formation of β-hydroxy sulphides *via* episulphonium ion intermediates[2] generated from arenesulphenyl halides,[3] or from reaction of organic disulphides with either lead(IV) salts[4] or trifluoroacetic anhydride.[5] All these studies have been concerned with the functionalisation of either hydrocarbons or remotely functionalised alkenes. We have extended the method of Trost *et al.* based on the use of lead(IV) salts to permit trifluoroacetoxysulphenylation[6,7] and hence the synthesis of hydroxy sulphides. In particular, as described elsewhere,[8,9] we find that manganese(III) salts can be used with advantage. This modification has permitted us to study the trifluoroacetoxysulphenylation of a wide variety of substituted alkenes. In the following papers we describe the reaction with unsaturated amides,[10] carboxylic acids,[10] and nitriles.[9] In this paper we describe the functionalisation of a variety of unsaturated esters derived from allylic, homoallylic, and other alcohols. In certain cases these reactions are characterised by a high degree of regiocontrol, as reported[11] in our preliminary communication.

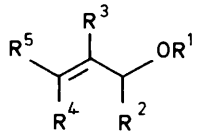
The results of the trifluoroacetoxysulphenylation of the esters are shown in the Table. The starting materials were obtained by acetylation or trifluoroacetylation of the appropriate alcohol in a routine manner. The formation of adducts was in each case achieved by reaction of the unsaturated ester with the appropriate disulphide in dichloromethane–trifluoroacetic acid in the presence of manganese(III) acetate dihydrate. Work-up afforded in each case crude trifluoroacetate adducts ($\nu_{max.}$ 1 790 cm^{-1}), which were then hydrolysed either under mild conditions in the case of the adducts of initial unsaturated trifluoroacetates (to afford diols) and of the adducts of some initial unsaturated

Table. Hydroxysulphenylation of allylic esters

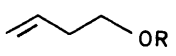
Alkene	Disulphide	Product(s)	Yield (%)[a]
CH_2=$CHCH_2OAc$ (**3**)	(**1**)	$PhSCH_2CH(OH)CH_2OAc$ (**17**)	71
		$PhSCH_2CH(OAc)CH_2OH$ (**30**)	11
CH_2=$CHCH_2O_2CCF_3$ (**4**)	(**1**)	$HOCH_2CH(SPh)CH_2OH$ (**24**)	98
CH_2=$CHCH_2OAc$ (**3**)[b]	(**2**)	$PrSCH_2CH(OH)CH_2OH$ (**19**)	64
		$HOCH_2CH(SPr)CH_2OH$ (**25**)	13
CH_2=$CHCH_2O_2CCF_3$ (**4**)	(**2**)	$HOCH_2CH(SPr)CH_2OH$ (**25**)	84
CH_2=$CHCHMeOAc$ (**5**)[c]	(**1**)	$PhSCH_2CH(OH)CHMeOH$ (**20**) and (**21**)	65
CH_2=$CHCHMeO_2CCF_3$ (**6**)[d]	(**1**)	$HOCH_2CH(SPh)CHMeOH$ (**26**) and (**27**)	98
CH_2=$CHCHPhO_2CCF_3$ (**7**)[e]	(**1**)	$HOCH_2CH(SPh)CHPhOH$ (**28**)	76
CH_3CH=$CHCH_2O_2CCF_3$ (**8**)	(**1**)	$CH_3CH(OH)CH(SPh)CH_2OH$ (**26**) and (**27**)	99
CH_2=$CEtCH_2OAc$ (**9**)	(**1**)	$PhSCH_2CEt(OH)CH_2OAc$ (**22**)	79
CH_2=$CEtCH_2O_2CCF_3$ (**10**)	(**1**)	$PhSCH_2CEt(OH)CH_2OH$ (**23**)	90
		$HOCH_2CEt(SPh)CH_2OH$ (**29**)	9
Me_2C=$CHCH_2O_2CCF_3$ (**11**)	(**1**)	$PhSCH_2CH(OH)CMe_2OH$ (**31**)	60
CH_2=$CH[CH_2]_2OAc$ (**13**)	(**1**)	$PhSCH_2CH(OH)[CH_2]_2OAc$ (**32**)	69
		$PhSCH_2CH(OAc)[CH_2]_2OH$ (**33**)	5
CH_2=$CHCH_2]_2O_2CCF_3$ (**14**)	(**1**)	$PhSCH_2CH(OH)[CH_2]_2OH$ (**34**)	40
		$HOCH_2CH(SPh)([CH_2]_2OH$ (**35**)	45
CH_2=$CH[CH_2]_3OAc$ (**15**)	(**1**)	$PhSCH_2CH(OH)[CH_2]_3OAc$ (**36**)	78
CH_2=$CH[CH_2]_3O_2CCF_3$ (**16**)	(**1**)	$PhSCH_2CH(OH)[CH_2]_3OH$ (**37**)	77

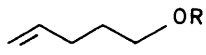
[a] Yields are based on products isolated after chromatographic separation. [b] Products separated after hydrolysis of intermediate monoacetates. [c] Inseparable mixture of diols characterised as acetals (see text). [d] Separable mixture of diols characterised as acetals (see text). [e] One diastereoisomer obtained (see text).

(1) R = Ph
(2) R = Pr
RSSR



(3) R^1 = $COCH_3$, R^2 = R^3 = R^4 = R^5 = H
(4) R^1 = $COCF_3$, R^2 = R^3 = R^4 = R^5 = H
(5) R^1 = $COCH_3$, R^2 = Me, R^3 = R^4 = R^5 = H
(6) R^1 = $COCF_3$, R^2 = Me, R^3 = R^4 = R^5 = H
(7) R^1 = $COCF_3$, R^2 = Ph, R^3 = R^4 = R^5 = H
(8) R^1 = $COCF_3$, R^2 = R^3 R^4 = H, R^5 = Me
(9) R^1 = $COCH_3$, R^2 = R^4 = R^5 = H, R^3 = Et
(10) R^1 = $COCF_3$, R^2 = R^4 = R^5 = H, R^3 = Et
(11) R^1 = $COCF_3$, R^2 = R^3 = H, R^4 = R^5 = Me
(12) R^1 = R^3 = R^4 = R^5 = H, R^2 = Ph





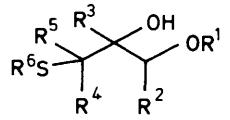
(13) R = $COCH_3$
(14) R = $COCF_3$
(15) R = $COCH_3$
(16) R = $COCF_3$

acetates (to afford hydroxyacetates), or under stronger conditions in the case of other acetates (to afford diols). In all cases, unless otherwise stated, products were isolated pure (t.l.c. and spectra) by chromatography, and in most cases were further characterised by preparation of the appropriate mono- or bis-4-nitrobenzoate.

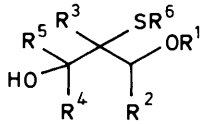
Addition of diphenyl disulphide (**1**) to allyl acetate (**3**) afforded two monoacetates (**17**) and (**30**) after work-up. The regiospecificity of the addition and the isolation of the minor product (**30**) give a clear indication of the origin of the regiocontrol. Although an episulphonium ion intermediate (**38**) might be expected to give products of Markovnikov addition (as observed) the isolation of the ester (**30**) shows a neighbouring group participation by the acetate leading to the intermediate ion (**39**). Collapse of this ion can then lead to both isolated products after work-up. The absence of acetyl migration on work-up was checked and the structure of the minor product (**30**) was confirmed by hydrolysis to the diol (**18**), which was also obtained from the major product (**17**).

In marked contrast, addition of diphenyl disulphide to allyl trifluoroacetate (**4**) afforded a single diol (**24**) after work-up. The regiospecific anti-Markovnikov nature of the addition is controlled by the powerful electron withdrawal of the trifluoroacetyl group. Neighbouring group participation to give an ion analogous to (**39**) is no longer favoured. Hence the inductive effect of the trifluoroacetoxy group determines the regiocontrol.

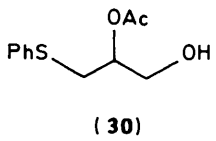
Additions of dipropyl disulphide (**2**) to allyl acetate (**3**) and trifluoroacetate (**4**) proceeded in a similar manner. After hydrolysis the acetate (**3**) afforded the diol (**19**) by Markovnikov addition as the major product, and the diol (**25**) by anti-Markovnikov addition as the minor product. The anti-Markovnikov product (**25**) was the only diol obtained from allyl trifluoroacetate (**4**). The isolation of a product of anti-Markovnikov addition to allyl acetate complicated the procedure for isolation of products so that it was not possible to observe acetyl migration in this case. The formation of a



(17) R^1 = $COCH_3$, R^2 = R^3 = R^4 = R^5 = H, R^6 = Ph
(18) R^1 = R^2 = R^3 = R^4 = R^5 = H, R^6 = Ph
(19) R^1 = R^2 = R^3 = R^4 = R^5 = H, R^6 = Pr
(20) R^1 = R^3 = R^4 = R^5 = H, R^2 = Me, R^6 = Ph(*erythro*)
(21) R^1 = R^3 = R^4 = R^5 = H, R^2 = Me, R^6 = Ph(*threo*)
(22) R^1 = $COCH_3$, R^2 = R^4 = R^5 = H, R^3 = Et, R^6 = Ph
(23) R^1 = R^2 = R^4 = R^5 = H, R^3 = Et, R^6 = Ph



(24) R^1 = R^2 = R^3 = R^4 = R^5 = H, R^6 = Ph
(25) R^1 = R^2 = R^3 = R^4 = R^5 = H, R^6 = Pr
(26) R^1 = R^3 = R^4 = R^5 = H, R^2 = Me, R^6 = Ph(*erythro*)
(27) R^1 = R^3 = R^4 = R^5 = H, R^2 = Me, R^6 = Ph(*threo*)
(28) R^1 = R^3 = R^4 = R^5 = H, R^2 = R^6 = Ph
(29) R^1 = R^2 = R^4 = R^5 = H, R^3 = Et, R^6 = Ph



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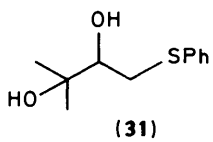

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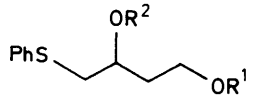
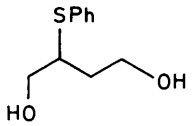
product of anti-Markovnikov addition in the reaction of allyl acetate with dipropyl disulphide (**2**) contrasts with the absence of such a product from diphenyl disulphide (**1**). The difference might be attributed to the great nucleophilicity of an alkylthio group relative to an aryl group. Such a factor might diminish the importance of neighbouring group participation.

Additions of diphenyl disulphide (**1**) to 1-methylallyl acetate (**5**) and trifluoroacetate (**6**) were characterised by high regio- but poor stereo-control. The mixture of diols (**20**) and (**21**) from the acetate (**5**) could not be separated but was converted into the mixture of acetals (**40**) and (**41**), which again was not separated. The diols (**26**) and (**27**) could be separated by chromatography, individually characterised and converted into their respective acetals (**42**) and (**43**). From the spectra of the mixture of acetals (**40**) and (**41**) the major isomer (**41**) could be recognised by the signals for 4-H at δ 3.74 and 5-H at 3.93; the minor isomer had signals at δ 4.21 for 4-H and δ 4.32 for 5-H. On the basis of literature precedent[12] the chemical shift differences permit structural assignments and hence the conclusion that the diols (**20**) and (**21**) were obtained in the ratio 1:3. In the case of the acetals (**42**) and (**43**) structures could be assigned readily by observation of the coupling constant $J_{4,5}$. In the case of the *trans*-acetal (**42**) formed from the diol (**26**) a large coupling ($J_{4,5}$ 11 Hz) was observed, characteristic of a *trans*-diequatorially substituted dioxolane. In the case of the *cis*-acetal (**43**) formed from the diol (**27**) a small coupling ($J_{4,5}$ < 3 Hz) was observed.

The analogous addition of diphenyl disulphide (**1**) to 1-phenylallyl trifluoroacetate (**7**) afforded a single diol (**28**), further characterised as the acetal (**44**). Again the stereochemistry of the acetal (**44**) could be assigned from the coupling



(32) $R^1 = COCH_3$, $R^2 = H$
(33) $R^1 = H$, $R^2 = COCH_3$
(34) $R^1 = R^2 = H$



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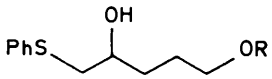
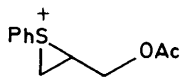


(36) $R = COCH_3$
(37) $R = H$



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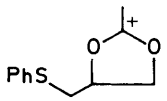

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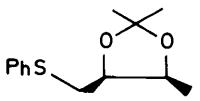

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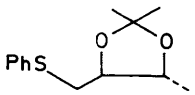

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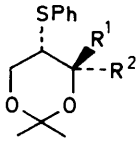
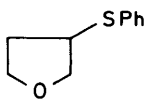


(42) $R^1 = Me$, $R^2 = H$
(43) $R^1 = H$, $R^2 = Me$
(44) $R^1 = Ph$, $R^2 = H$



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constant $J_{4,5}$ (11 Hz), indicative of the *trans*-diequatorially substituted dioxolane. Thus whilst addition to the acetate (**5**) proceeds with Markovnikov regiospecificity and little stereoselectivity, addition to the trifluoroacetate (**7**) proceeds with both anti-Markovnikov regiospecificity and stereospecificity, in contrast to the addition to the trifluoroacetate (**6**) which proceeds with anti-Markovnikov regiospecificity but little stereoselectivity. The most likely explanation for the high stereocontrol in addition to (**7**) is kinetic control of the face of attack of the sulphur electrophile on the alkene. Addition of diphenyl disulphide (**1**) to but-2-enyl trifluoroacetate (**8**) again proceeds regiospecifically to give after hydrolysis the same diols (**26**) and (**27**) as isolated from addition to the ester (**6**). Thus addition to this ester (**8**) is also characterised by low stereoselectivity.

Addition to the acetate (**9**) afforded a single acetate product (**22**), further characterised by hydrolysis to the diol (**23**). This diol (**23**) was obtained as the major product from the trifluoroacetate (**10**), showing that in such a compound the effect of the trifluoroacetate group is insufficient to control the regiochemistry. However a small amount of the minor diol (**29**) was found in the product mixture.

The attempted addition of diphenyl disulphide (**1**) to the trifluoroacetate (**11**) afforded after hydrolysis the diol (**31**) as the only product. This diol is most probably formed *via* solvolytic rearrangement under the acidic reaction conditions prior to addition.

The effect of separating the ester function from the double bond was examined in a representative homoallylic acetate (**13**) and trifluoroacetate (**14**). As expected, Markovnikov addition to the acetate (**13**) afforded as the major product the adduct (**32**), isolated after mild hydrolysis, and characterised as the diol (**34**). However a minor product was the acetate (**33**), isolated after mild hydrolysis. The isolation of this minor product shows that in the case of a homoallylic acetate too neighbouring group participation occurs and can control the regiochemistry. In the case of addition to the trifluoroacetate (**14**) two diols (**34**) and (**35**) were obtained in 40 and 45% yield, respectively. The former (**34**) was identical with the hydrolysis product from the acetate (**13**). Hence the trifluoroacetate group, even in a homoallylic ester, exerts a powerful regiocontrol, as shown by the formation of the anti-Markovnikov adduct (**35**) in 45% yield. Further separation of the ester functions from the double bond was examined in addition to the esters (**15**) and (**16**). In those systems the influence of the ester group was substantially removed. The acetate (**15**) gave the Markovnikov product, isolated as the acetate (**36**) and converted into the diol (**37**). Similarly, after addition and work-up, the trifluoroacetate ester (**16**) afforded the same diol (**37**), indicating an absence of regiocontrol by the ester substituent.

Although our major interest in these results relates to the understanding of substituent effects in the control of additions to substituted alkenes, our programme of synthesis of sulphenylated heterocyclic systems[8–10] suggested the use of diols in the synthesis of oxygen heterocycles. We found that under Mitsunobu[13] conditions the mixture of diols (**34**) and (**35**) was converted in 74% yield into 3-(phenylthio)tetrahydrofuran (**45**).

Our observations of neighbouring group participation in additions to both allylic and homoallylic esters are unexceptional. In the halogenation of allyl alcohols and allyl esters earlier studies[14] thoroughly document such effects. More recently[15] observations of the 1,3-addition of tellurium tetrachloride to allylic esters have implied ester participation, probably *via* an intermediate similar to the ion (**39**). Again recent studies[16] have established that in addition of halogen derivatives to homoallylic acetates neighbouring group participation controls the nature of the products.

Our results with allylic trifluoroacetates show that the large substituent effect controls the regiochemistry of the reaction. Even in the case of the homoallylic ester (**13**) a strong substituent effect profoundly influences the nature of the products. To our knowledge, our use of trifluoroacetate esters to control regiochemistry in additions to substituted alkenes has no literature precedent. Engman,[15] in a related study, investigated the addition of tellurium tetrachloride to allyl trichloroacetate but found that no reaction occurred. As the conversions of allylic alcohols into their trifluoroacetate esters and the later hydrolysis of adducts to alcohol products are generally straightforward, we believe that our specific illustration of the control of regiochemistry by trifluoroacetate esters in the formation of adducts by trifluoroacetoxysulphenylation may have a much wider generality. In particular, such control is to be expected in the use of other electrophiles.

Experimental

General experimental details have been described earlier.[6] Unless otherwise stated ^1H and ^{13}C n.m.r. spectra were recorded with a Bruker 360 AM spectrometer and mass spectra were recorded at 70 eV with a Kratos MS 30 spectrometer fitted with a Digispec D5 50S data system. All solid compounds were microanalysed at University College, London. All oils unless otherwise indicated were observed to be homogeneous (t.l.c.).

Preparation of Alcohols.—1-Phenylprop-2-en-1-ol (**12**) was obtained by reaction of vinylmagnesium bromide with benzaldehyde in tetrahydrofuran and was isolated in 52% yield after

work-up and distillation as a colourless liquid, b.p. 107 °C at 16 mmHg. All other alcohols were obtained from commercial sources.

Preparation of Trifluoroacetates.—The alcohol (10 mmol) was stirred at 0 °C in dichloromethane (50 ml) containing trifluoroacetic anhydride (20 mmol) for 7 h. Removal of volatile material by careful distillation under reduced pressure afforded as a residue the trifluoroacetate, which was used directly.

Preparation of Acetates.—The alcohol (10 mmol) was stirred at room temperature in pyridine (20 ml) containing acetic anhydride (20 mmol) and 4-dimethylaminopyridine (50 mg) for 10 h. The mixture was poured into water, neutralised with sodium hydrogen carbonate, and extracted with ether (3 × 30 ml). The combined extracts were washed with saturated aqueous copper sulphate (4 × 30 ml) and then with water (3 × 30 ml). The ethereal solution was dried and evaporated under reduced pressure to give the acetate, which was used directly.

General Procedure for Trifluoroacetoxysulphenylation of Unsaturated Esters.—The appropriate disulphide (23.7 mmol) was added at 0 °C to a stirred solution of manganese(III) acetate dihydrate (1.48 g, 5.5 mmol) in dichloromethane (50 ml) containing trifluoroacetic acid (5 ml). The unsaturated compound (7.5 mmol) in a little dichloromethane was quickly added and the solution was stirred for 8 h, poured into water (50 ml), and extracted with ether (3 × 50 ml). The organic phase was washed with aqueous potassium hydrogen carbonate (3 × 50 ml) and then water (3 × 50 ml), dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give a crude product.

Hydrolysis of Trifluoroacetates.—The crude trifluoroacetate was dissolved in the minimum amount of ether and stirred at room temperature for 18 h with aqueous sodium carbonate (15%; 30 ml). The mixture was partitioned between ether and water and the aqueous phase further extracted with ether (2 × 50 ml). The combined organic extracts were washed with water (3 × 50 ml), dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography.

Hydrolysis of Acetates.—The acetate was dissolved in methanol (30 ml) containing added sodium hydroxide. The solution was heated under reflux for 30 min and then concentrated under reduced pressure. The residue was partitioned between ether and water and the aqueous phase further extracted with ether (3 × 50 ml). Work-up as before and purification by column chromatography afforded the alcohol.

Addition of Diphenyl Disulphide to Allyl Acetate.—As in the general procedure diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of allyl acetate (0.74 g). Work-up, hydrolysis of the crude product with sodium carbonate, and purification by chromatography afforded as the less polar fraction *2-hydroxy-3-phenylthiopropyl acetate* (**17**) (0.65 g, 71% w.r.t. diphenyl disulphide); $\nu_{max.}(CHCl_3)$ 3 475, 1 740, and 1 590 cm^{-1}; δ_H 2.01 (3 H, s, CH_3), 2.99 (1 H, dd, *J* 14 and 7 Hz) and 3.07 (1 H, dd, *J* 14 and 6 Hz) (CH_2S), 3.48 (1 H, s, OH), 3.93 (1 H, m, C*H*OH), 4.09 (1 H, dd, *J* 11 and 6 Hz) and 4.18 (1 H, dd, *J* 11 and 4 Hz) (CH_2OAc), and 7.15—7.4 (5 H, complex, aromatic); δ_C 20.49 (CH_3), 37.59 (CH_2S), 66.59 (CH_2OAc), 68.04 (CHO), 126.43, 128.88, 129.72, and 135.15 (aromatic carbon), and 170.86 (CO); and as the more polar fraction *1-hydroxymethyl-2-phenylthioethyl acetate* (**30**) (100 mg, 11% w.r.t. diphenyl disulphide) (Found: M^+, 226.0694. $C_{11}H_{14}O_2S$ requires *M*, 226.0664); $\nu_{max.}(CHCl_3)$ 3 480, 1 745, and 1 590 cm^{-1}; δ_H 2.00 (3 H, s, CH_3), 2.85 (1 H, s, OH), 3.18 (2 H, d, *J* 6 Hz, CH_2S), 3.78 (2 H, d, *J* 5 Hz, CH_2O), 5.01 (1 H, m, CHO), and 7.15—7.45 (5 H, complex, aromatic); δ_C 20.82 (CH_3), 33.90 (CH_2S), 62.75 (CH_2OH), 73.75 (*C*H_2OAc), 126.48, 128.99, 129.72, and 135.48 (aromatic carbon), and 170.76 (CO).

Both the acetates (**17**) and (**30**) on hydrolysis with potassium hydroxide in methanol afforded quantitatively 3-phenylthiopropane-1,2-diol (**18**), m.p. 71 °C (lit.,[17] 72—73 °C) (from ether–light petroleum) (Found: C, 58.6; H, 6.5; S, 17.4. Calc. for $C_9H_{10}O_2S$: C, 58.7; H, 6.5; S, 17.4); $\nu_{max.}(CHCl_3)$ 3 440 and 1 595 cm^{-1}; δ_H 2.97 (1 H, dd, *J* 14 and 7 Hz) and 3.04 (1 H, dd, *J* 14 and 5 Hz) (CH_2S), 3.42 (1 H, s, OH), 3.48 (1 H, s, OH), 3.54 (1 H, dd, *J* 12 and 3 Hz), and 3.71 (1 H, dd, *J* 12 and 3 Hz) (CH_2OH), 3.77 (1 H, m, CHOH), and 7.15—7.5 (5 H, complex, aromatic); δ_C 37.87 (CH_2S), 65.31 (CH_2OH), 70.33 (CHOH), and 126.80, 129.21, 130.14, and 132.62 (aromatic).

Addition of Diphenyl Disulphide to Allyl Trifluoroacetate.—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in dichloromethane (50 ml) containing trifluoroacetic acid (10 ml) and allyl trifluoroacetate (1.2 g). The mixture was initially maintained at 0 °C and then was stirred at room temperature for 18 h. The solution was poured into aqueous sodium carbonate and extracted with ether (3 × 50 ml). The organic phase was washed with aqueous sodium carbonate (2 × 50 ml) and then water (3 × 50 ml), dried ($MgSO_4$), filtered, and evaporated under reduced pressure. Hydrolysis of the crude product with sodium carbonate and purification of the product by column chromatography [eluant ethyl acetate–light petroleum (1 : 1)] afforded as a colourless oil 2-phenylthiopropane-1,3-diol (**24**) (0.67 g, 98% w.r.t. diphenyl disulphide); $\nu_{max.}(CHCl_3)$ 3 440 and 1 595 cm^{-1}; δ_H 3.29 (1 H, m, CHS), 3.65 (2 H, br s, OH), 3.78 (4 H, m, CH_2), and 7.2—7.45 (5 H, complex, aromatic); δ_C 52.91 (CHS), 63.02 (CH_2) and 126.61, 127.58, 129.17, and 132.42 (aromatic carbon). The diol (**24**) was further characterised as the bis-*p*-nitrobenzoate, m.p. 96 °C (from ether) (lit.,[18] 95—96 °C).

Addition of Dipropyl Disulphide to Allyl Acetate.—Dipropyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of allyl acetate (0.74 g). Work-up, hydrolysis of the crude product with sodium hydroxide in methanol, and subsequent purification by chromatography afforded as a colourless oil a mixture of 3-propylthiopropane-1,2-diol (**19**) and 2-propylthiopropane-1,3-diol (**25**) (479 mg, 77% w.r.t. dipropyl disulphide) in 5:1 ratio (^1H and ^{13}C n.m.r.); $\nu_{max.}$(neat) 3 400 cm^{-1}; δ_H 0.99 (3 H, t, *J* 7 Hz, CH_3), 1.62 (2 H, m, CH_2), 2.53 (2 H, t, *J* 7 Hz, CH_2S), 2.59 [1 H (major isomer), dd, *J* 14 and 8 Hz) and, 2.67 [1 H (major isomer), dd, *J* 14 and 5 Hz] (CH_2S), 2.88 [1 H (minor isomer), q, *J* 7 Hz, CHS], and 3.4—3.85 [5 H (major isomer), complex, CH_2O, CHO, and OH; and 6 H (minor isomer), complex, CH_2 and OH]; δ_C 13.33 (CH_3), 23.02 (CH_2 of major isomer), 23.47 (CH_2 of minor isomer), 33.24 (CH_2 of minor isomer), 34.71 (CH_2 of major isomer), 35.74 (CH_2 of major isomer), 50.15 (CH of minor isomer), 63.19 (CH_2 of minor isomer), 65.45 (CH_2 of major isomer), and 70.65 (CH of major isomer).

Addition of Dipropyl Disulphide to Allyl Trifluoroacetate (**4**).—Dipropyl disulphide (0.55 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of allyl trifluoroacetate (1.2 g). Work-up, hydrolysis of the crude product with sodium carbonate, and purification by chromatography afforded as a colourless oil *2-propylthiopropane-1,3-diol* (**25**) (0.51 g, 84% w.r.t. dipropyl disulphide); $\nu_{max.}$(neat) 3 400 cm^{-1}; δ_H 1.00 (3 H, t, *J* 7 Hz, CH_3), 1.62 (2 H, m, CH_2), 2.54 (2 H, t,

J 7 Hz, CH_2S), 2.87 (1 H, m, CHS), and 3.7—3.9 (6 H, complex, CH_2O and OH); δ_C 13.26 (CH_3), 23.34 (CH_2), 33.12 (CH_2S), 49.77 (CHS), and 63.04 (CH_2OH). The diol (**25**) was further characterised as the *bis*-p-*nitrobenzoate*, m.p. 100—102 °C (from ethyl acetate–light petroleum) (Found: C, 53.5; H, 4.5; N, 6.2; S, 7.1. $C_{20}H_{20}N_2O_8S$ requires C, 53.6; H, 4.5; N, 6.2; S, 7.1%).

Addition of Diphenyl Disulphide to 1-Methylallyl Acetate (**5**).—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of the acetate (**5**) (0.54 g). Work-up, hydrolysis of the crude product with sodium carbonate, and subsequent purification by chromatography afforded as a colourless oil a mixture of *erythro*- and *threo*-3-phenylthiobutane-1,2-diols (**20**) and (**21**) (480 mg, 65% w.r.t. diphenyl disulphide) in the ratio 1:3; $\nu_{max.}(CHCl_3)$ 3 445 and 1 595 cm^{-1}; δ_H 1.2 (3 H, complex, CH_3), 2.95—3.95 (complex), and 7.15—7.4 (5 H, complex, aromatic); δ_C 17.67 (CH_3 of minor isomer), 19.52 (CH_3 of major isomer), 37.04 (CH_2 of minor isomer), 38.37 (CH_2 of major isomer, 69.33 (CH of major isomer), 69.51 (CH of minor isomer), 72.99 (CH of minor isomer), 73.63 (CH of major isomer), and aromatic carbon signals.

Addition of Diphenyl Disulphide to 1-Methylallyl Trifluoroacetate (**6**).—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of the trifluoroacetate (**6**) (1.3 g). Work-up, hydrolysis of the crude product with sodium carbonate, and subsequent purification by chromatography afforded (as the less polar fraction) as a colourless oil, *threo*-2-phenylthiobutane-1,3-diol (**27**) (469 mg, 64% w.r.t. diphenyl disulphide); $\nu_{max.}(CHCl_3)$ 3 430 and 1 590 cm^{-1}; δ_H 1.38 (3 H, d, *J* 7 Hz, CH_3), 3.16 (1 H, m, CH), 3.41 (2 H, br, OH), 3.82 (1 H, dd, *J* 17 and 6 Hz), and 3.91 (1 H, m) (CH_2OH), 4.02 (1 H, m, CHOH), and 7.2—7.45 (5 H, complex, aromatic); δ_C 21.36 (CH_3), 58.07 (CHS), 63.12 (CH_2OH), 69.43 (CHOH), and 127.44, 129.19, 132.16, and 134.45 (aromatic carbon); [*bis*-p-*nitrobenzoate*, m.p. 103 °C (from ether–light petroleum) (Found: C, 58.0; H, 4.1; N, 5.4; S, 6.4. $C_{24}H_{20}N_2O_8S$ requires C, 58.1; H, 4.0; N, 5.65; S, 6.45%)]; and (as the more polar fraction) erythro-2-*phenylthiobutane*-1,3-*diol* (**26**) (252 mg, 34% w.r.t. diphenyl disulphide); $\nu_{max.}(CHCl_3)$ 3 445 and 1 590 cm^{-1}; δ_H 1.36 (3 H, d, *J* 7 Hz, CH_3), 3.18 (1 H, m, CHS), 3.42 (2 H, br, OH), 3.76 (1 H, dd, *J* 11 and 5 Hz) and 3.87 (1 H, dd, *J* 11 and 7 Hz) (CH_2OH), 4.13 (1 H, m, CHOH), and 7.18—7.48 (5 H, complex, aromatic); δ_C 20.38 (CH_3), 58.92 (CHS), 63.09 (CH_2OH), 68.41 (CHOH), and 127.29, 129.16, 131.97, and 134.55 (aromatic carbon); [*bis*-p-*nitrobenzoate*, m.p. 141 °C (from ethyl acetate–light petroleum) (Found: C, 58.0; H, 4.2; N, 5.5; S, 6.3. $C_{24}H_{20}N_2O_8S$ requires C, 58.1; H, 4.0; N, 5.65; S, 6.45%)].

Addition of Diphenyl Disulphide to 1-Phenylallyl Trifluoroacetate (**7**).—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of the trifluoroacetate (**7**) (1.79 g). Work-up, hydrolysis of the crude product with sodium carbonate, and purification by chromatography afforded as a colourless oil 1-*phenyl*-2-*phenylthiopropane*-1,3-*diol* (**28**) (0.73 g, 76% w.r.t. diphenyl disulphide); $\nu_{max.}(CHCl_3)$ 3 530 and 1 590 cm^{-1}; δ_H 3.36 (2 H, complex, CHS and OH), 3.69 (1 H, dd, *J* 12 and 6 Hz) and 3.78 (1 H, dd, *J* 12 and 5 Hz) (CH_2O), 3.99 (1 H, br s, OH), 4.83 (1 H, d, *J* 6 Hz, C*H*OH), and 7.1—7.4 (5 H, complex, aromatic); δ_C 57.72 (CHS), 62.60 (CH_2OH), 75.68 (CHOH), and 126.41, 127.33, 127.81, 128.28, 129.00, 132.21, 134.07, and 141.52 (aromatic carbon); [*bis*-p-*nitrobenzoate*, m.p. 154—156 °C (from ether–light petroleum) (Found: C, 62.05; H, 4.1; N, 5.1; S, 5.6. $C_{29}H_{22}N_2O_8S$ requires C, 62.4; H, 3.9; N, 5.0; S, 5.7%)].

Addition of Diphenyl Disulphide to But-2-enyl Trifluoroacetate (**8**).—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of the trifluoroacetate (**8**) (1.3 g). Work-up, hydrolysis of the crude product with sodium carbonate, and subsequent purification by chromatography afforded (as the less polar fraction) as a colourless oil *threo*-2-phenylthiobutane-1,3-diol (**27**) (490 mg, 66% w.r.t. diphenyl disulphide), identical with the sample isolated from the trifluoroacetate (**6**); and (as the more polar fraction) as a colourless oil *erythro*-2-phenylthiobutane-1,3-diol (**26**) (240 mg, 33% w.r.t. diphenyl disulphide) identical with the sample isolated from the trifluoroacetate (**6**).

Addition of Diphenyl Disulphide to 2-Ethylallyl Acetate (**9**).—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of the acetate (**9**) (0.95 g). Work-up, hydrolysis of the crude product with sodium carbonate, and subsequent purification by chromatography afforded as a colourless oil 2-*ethyl*-2-*hydroxy*-3-*phenylthiopropyl acetate* (**22**) (745 mg; 79% w.r.t. diphenyl disulphide); $\nu_{max.}(CHCl_3)$ 3 465, 1 740, and 1 595 cm^{-1}; δ_H 0.90 (3 H, t, *J* 7 Hz, CH_3), 1.63 (2 H, q, *J* 7 Hz, CH_2), 1.95 (3 H, s, $COCH_3$), 2.93 (1 H, s, OH), 3.13 (2 H, m, CH_2S), 4.03 (2 H, m, CH_2O), and 7.1—7.45 (5 H, complex, aromatic); δ_C 7.12 (CH_3), 20.39 (CH_3CO), 29.07 (CH_2), 41.60 (CH_2S), 67.61 (CH_2O), 73.29 (quaternary C), 126.23, 128.75, 129.79, and 136.52 (aromatic carbon), and 170.43 (CO). The alcohol (**22**) was further characterised by hydrolysis to the diol (**23**) and conversion into the *bis*-p-*nitrobenzoate*, m.p. 128 °C (from ether) (Found: C, 58.6; H, 4.3; N, 5.4; S, 6.1. $C_{25}H_{22}N_2O_8S$ requires C, 58.8; H, 4.3; N, 5.5; S, 6.3%).

Addition of Diphenyl Disulphide to 2-Ethylallyl Trifluoroacetate (**10**).—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of the trifluoroacetate (**10**) (1.33 g). Work-up, hydrolysis of the crude product with sodium carbonate, and subsequent purification by chromatography afforded as a mixture 2-ethyl-3-phenylthiopropane-1,2-diol (**23**) and 2-ethyl-2-phenylthiopropane-1,3-diol (**29**) (767 mg, 99% yield w.r.t. diphenyl disulphide; ratio (10:1); $\nu_{max.}$(neat) 3 420 and 1 590 cm^{-1}; ^1H and ^{13}C n.m.r. of the major isomer (**23**) as already listed under the addition of diphenyl disulphide to the acetate (**9**); for the minor isomer (**29**) δ_H 1.00 (3 H, t, *J* 7 Hz, CH_3), 1.45 (2 H, q, *J* 7 Hz, CH_2), 3.53 (6 H, complex, CH_2 and OH), and aromatic signals; δ_C 8.55 (CH_3), 25.36 (CH_2), 59.90 (quaternary C), 65.63 (CH_2O), and 126.92, 129.45, 129.82, and 137.61 (aromatic carbon).

Addition of Diphenyl Disulphide to 3-Methylbut-2-enyl Trifluoroacetate (**11**).—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of the trifluoroacetate (**11**) (1.32 g). Work-up, hydrolysis of the crude product with sodium carbonate, and subsequent purification by chromatography afforded as a colourless oil 3-*methyl*-1-*phenylthiobutane*-2,3-*diol* (**31**) (470 mg, 60% w.r.t. diphenyl disulphide); $\nu_{max.}(CHCl_3)$ 3 580 and 1 590 cm^{-1}; δ_H 1.15 (3 H, s, CH_3), 1.19 (3 H, s, CH_3), 2.85 (1 H, m) and 3.20 (1 H, m) (CH_2S), 3.14 (1 H, br s, OH), 3.45 (1 H, m, CHOH), 3.67 (1 H, s, OH), and 7.1—7.4 (5 H, complex, aromatic); δ_C 24.40 (CH_3), 26.4 (CH_3), 37.38 (CH_2S), 72.39 (CCH_3), and 126.41, 128.94, 129.80, and 135.49 (aromatic carbon); [*bis*-p-*nitrobenzoate*, m.p. 162 °C (from ether) (Found: C, 58.6; H, 4.5; N, 5.4; S, 6.4. $C_{25}H_{22}N_2O_8S$ requires C, 58.8; H, 4.3; N, 5.5; S, 6.3%)].

Addition of Diphenyl Disulphide to But-3-enyl Acetate (**13**).—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of the acetate (**13**) (0.84 g). Work-up, hydrolysis of the crude product with sodium

carbonate, and subsequent purification by chromatography afforded as a colourless oil (the less polar fraction) 3-*hydroxy*-4-*phenylthiobutyl acetate* (**32**) (617 mg, 69% w.r.t. diphenyl disulphide); $\nu_{max.}(CCl_4)$ 3 545, 1 745, and 1 590 cm^{-1}; δ_H 1.7—2.0 (2 H, m, CH_2CHO), 1.99 (3 H, s, CH_3), 2.97 (1 H, dd, *J* 14 and 8 Hz) and 3.07 (1 H, dd, *J* 14 and 5 Hz) (CH_2S), 3.35 (1 H, br s, OH), 3.82 (1 H, m, CHOH), 4.20 (2 H, m, CH_2OAc), and 7.1—7.4 (5 H, complex, aromatic); δ_C 20.49 (CH_3), 34.72 (CH_2CHO), 41.34 (CH_2S), 61.14 (CH_2OAc), 66.71 (CHOH), 128.11, 128.71, 129.49, and 135.49 (aromatic carbon), and 170.84 (CO). The alcohol (**32**) was hydrolysed to give 1-phenylthiobutane-2,4-diol (**34**), characterised as the *bis*-p-*nitrobenzoate*, m.p. 91 °C (from ether) (Found: C, 57.9; H, 4.0; N, 5.7; S, 6.4. $C_{24}H_{20}N_2O_8S$ requires C, 58.0; H, 4.0; N, 5.6; S, 6.4%); and (as the more polar fraction) 3-*hydroxy*-1-(*phenylthiomethyl*)*butyl acetate* (**33**) (44 mg, 5% w.r.t. diphenyl disulphide); $\nu_{max.}(CCl_4)$ 3 550, 1 750, and 1 590 cm^{-1}; δ_H 1.75—2.05 (2 H, m, CH_2CO), 2.00 (3 H, s, CH_3), 2.25 (1 H, br s, OH), 3.09 (1 H, dd, *J* 14 and 5 Hz) and 3.17 (1 H, dd, *J* 14 and 7 Hz) (CH_2S), 3.52—3.70 (2 H, m, CH_2OH), 5.17 (1 H, m, CHOAc), and 7.15—7.4 (5 H, complex, aromatic). The alcohol (**33**) was hydrolysed to give 1-phenylthiobutane-2,4-diol (**34**), characterised as already described.

Addition of Diphenyl Disulphide to But-3-enyl Trifluoroacetate (**14**).—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of the trifluoroacetate (**14**) (1.2 g). Work-up, hydrolysis of the crude product with sodium carbonate, and subsequent purification by chromatography afforded (as the less polar fraction) as a colourless oil 1-*phenylthiobutane*-2,4-*diol* (**34**) (296 mg, 40% w.r.t. diphenyl disulphide); $\nu_{max.}(CHCl_3)$ 3 480 and 1 590 cm^{-1}; δ_H 1.65—1.85 (2 H, m, CH_2), 2.94 (1 H, dd, *J* 14 and 8 Hz) and 3.07 (1 H, dd, *J* 14 and 5 Hz) (CH_2S), 3.09 (1 H, br s, OH), 3.56 (1 H, s, OH), 3.7—3.85 (2 H, complex, CH_2O), 3.91 (1 H, m, CHO), and 7.15—7.45 (5 H, complex, aromatic); δ_C 37.50 (CH_2), 41.38 (CH_2S), 60.21 (CH_2O), 69.01 (CHOH), and 126.23, 128.92, 132.08, and 133.84 (aromatic carbon), further characterised as the bis-*p*-nitrobenzoate, m.p. 91 °C (from ether) (already described). Further elution (ether) afforded as the more polar fraction (as a colourless oil) 2-*phenylthiobutane*-1,4-*diol* (**35**) (329 mg, 45% w.r.t. diphenyl disulphide); $\nu_{max.}(CHCl_3)$ 3 420 and 1 590 cm^{-1}; δ_H 1.8—2.0 (2 H, complex, CH_2), 3.08 (2 H, br, OH), 3.35 (1 H, m, CHS), 3.62 (1 H, dd, *J* 11 and 6 Hz) and 3.68 (1 H, dd, *J* 11 and 5 Hz) (CH_2O), 3.75—3.9 (2 H, complex, CH_2OH), and 7.2—7.5 (5 H, complex, aromatic); δ_C 34.59 (CH_2), 48.28 (CHS), 59.81 (CH_2OH), 64.45 (CH_2OH), and 126.25, 127.14, 129.48, and 135.70 (aromatic); [*bis*-p-*nitrobenzoate*, m.p. 106 °C (from ether–light petroleum) (Found: C, 58.3; H, 4.0; N, 5.6; S, 6.6. $C_{24}H_{20}N_2O_8S$ requires C, 58.0; H, 4.0; N, 5.6; S, 6.45%)].

Addition of Diphenyl Disulphide to Pent-4-enyl Acetate (**15**).—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of the acetate (**15**) (0.95 g). Work-up, hydrolysis of the crude product with sodium carbonate, and subsequent purification by chromatography afforded as a colourless oil 4-*hydroxy*-5-*phenylthiopentyl acetate* (**36**) (0.73 g, 78% w.r.t. diphenyl disulphide); $\nu_{max.}(CHCl_3)$ 3 540, 1 745, and 1 590 cm^{-1}; δ_H 1.5—1.85 (4 H, complex, CH_2CH_2CO), 2.00 (3 H, s, CH_3), 2.89 (1 H, m) and 3.08 (1 H, m) (CH_2S), 3.08 (1 H, br, OH), 3.68 (1 H, m, CHO), 4.03 (2 H, t, *J* 7 Hz, CH_2O), and 7.15—7.45 (5 H, complex, aromatic); δ_C 20.70 (CH_3), 24.84 (CH_2), 32.41 (CH_2), 41.95 (CH_2S), 64.22 (CH_2O), 69.20 (CHO), 126.38, 128.91, 129.83, and 135.62 (aromatic carbon), and 170.88 (CO); further characterised by hydrolysis to the diol (**37**) and conversion into the *bis*-p-*nitrobenzoate*, m.p. 101 °C (from ether–light petroleum) (Found: C, 58.9; H, 4.5; N, 5.4; S, 6.4. $C_{25}H_{22}H_2O_8S$ requires C, 58.8; H, 4.3; N, 5.5; S, 6.3%).

Addition of Diphenyl Disulphide to Pent-4-enyl Trifluoroacetate (**16**).—Diphenyl disulphide (0.81 g) was oxidised by manganese(III) acetate dihydrate (1.48 g) in the presence of the trifluoroacetate (**16**) (1.3 g). Work-up, hydrolysis of the crude product with sodium carbonate, and subsequent purification by chromatography afforded as a colourless oil 1-phenylthiopentane-2,5-diol (**37**) (582 mg, 77% w.r.t. diphenyl disulphide); $\nu_{max.}(CHCl_3)$ 3 420 and 1 590 cm^{-1}; δ_H 1.48—1.74 (4 H, complex), 2.92 (1 H, dd, *J* 14 and 8 Hz) and 3.04 (1 H, dd, *J* 14 and 5 Hz) (CH_2S), 3.58 (2 H, m, CH_2OH), 3.69 (1 H, m, CHOH), 3.88 (2 H, br s, OH), and 7.1—7.4 (5 H, complex, aromatic); δ_C 28.90 and 33.08 (CH_2), 41.90 (CH_2S), 62.54 (CH_2OH), 69.80 (CHOH), and 126.43, 129.02, 129.87, and 135.85 (aromatic carbon); further characterised as the bis-*p*-nitrobenzoate, m.p. 101 °C (from ether–light petroleum) (already described).

Preparation of Acetals.—The diol (100 mg) was stirred at room temperature for 1 h in 2,2-dimethoxypropane (10 ml) in the presence of Amberlyst 15 ion-exchange resin as catalyst. The mixture was filtered and the filtrate stirred with solid potassium carbonate (0.5 g) for 5 min. Further filtration, evaporation of the filtrate under reduced pressure, and purification of the residue by column chromatography [eluant ethyl acetate–light petroleum (b.p. 40—60 °C)] afforded the acetal.

By this procedure *erythro*-2-phenylthiobutane-1,3-diol (**26**) (100 mg) gave as a colourless oil trans-2,2,6-*trimethyl*-5-*phenylthio*-1,3-*dioxolane* (**42**), δ_H 1.37 (3 H, d, *J* 7 Hz, CH_3), 1.38 (3 H, s, CH_3), 1.39 (3 H, s, CH_3), 2.95 (1 H, dt, *J* 11, 11, and 5 Hz, 5-H), 3.75 (1 H, q, *J* 12 and 11 Hz, 4*ax*-H), 3.83 (1 H, m, 6-H), 3.88 (1 H, q, *J* 12 and 5 Hz, 4*eq*-H), and 7.15—7.45 (5 H, complex, aromatic); δ_C 19.5 (CH_3), 20.5 (CH_3), 29.9 (CH_3), 49.1 (C-5), 64.7 (CH_2), 69.5 (C-6), 98.9 (C-2), and aromatic resonances.

threo-2-Phenylthiobutane-1,3-diol (**27**) (100 mg) gave as a colourless oil cis-2,2,6-*trimethyl*-5-*phenylthio*-1,3-*dioxolane* (**43**), δ_H 1.34 (3 H, d, *J* 7 Hz, CH_3), 1.46 (3 H, s, CH_3), 1.49 (3 H, s, CH_3), 3.02 (1 H, m, 5-H), 3.97 (1 H, dd, *J* 12 and 2 Hz, 4-H), 4.22 (1 H, dd, *J* 12 and 2.5 Hz, 4-H), 4.34 (1 H, m, 6-H), and 7.15—7.45 (5 H, complex, aromatic); δ_C 19.57 (CH_3), 20.06 (CH_3), 28.26 (CH_3), 51.26 (C-5), 65.22 (CH_2), 67.65 (C-6), 99.19 (C-2), and aromatic resonances.

erythro-1-Phenyl-2-phenylthiopropane-1,3-diol (**28**) (150 mg) gave as a colourless oil trans-2,2,6-*trimethyl*-5-*phenylthio*-1,3-*dioxolane* (**44**), δ_H 1.47 (3 H, s, CH_3), 1.53 (3 H, s, CH_3), 3.28 (1 H, dt, *J* 11, 11, and 5 Hz, 5-H), 3.93 (1 H, q, *J* 12 and 11 Hz, 4*ax*-H), 4.04 (1 H, q, *J* 12 and 5.5 Hz, 4*eq*-H), 4.70 (1 H, d, *J* 11 Hz, 6-H), and 7.0—7.5 (10 H, complex, aromatic); δ_C 19.12 (CH_3), 29.50 (CH_3), 49.15 (C-5), 64.76 (CH_2), 76.41 (C-6), 99.15 (C-2), and aromatic resonances.

Acetals (**40**) *and* (**41**) *from the* 1-*Phenylthiobutane*-2,3-*diols* (**20**) *and* (**21**).—By the foregoing procedure the mixture of 1-phenylthiobutane-2,3-diols (**20**) and (**21**) gave as a colourless oil a mixture of acetals (**40**) and (**41**). The major *trans*-isomer (**41**) showed δ_H 1.32 (3 H, d, CH_3), 1.39 (6 H, s, CH_3), 3.06 (1 H, dd, *J* 13 and 6 Hz) and 3.19 (1 H, dd, *J* 13 and 6 Hz) (CH_2S), 3.74 (1 H, m, 4-H), 3.93 (1 H, m, 5-H), and 7.15—7.45 (5 H, complex, aromatic); δ_C 18.36 (CH_3), 27.15 (CH_3), 27.47 (CH_3), 36.41 (CH_2), 77.14 (CH), 80.89 (CH), 108.64 (C-2), and aromatic resonances. The minor *cis*-isomer (**40**) showed δ_H 1.24 (3 H, d, CH_3), 1.39 (3 H, s, CH_3), 1.46 (3 H, s, CH_3), 2.97 (1 H, dd, *J* 13 and 6.5 Hz) and 3.08 (1 H, dd, *J* 13 and 6.5 Hz) (CH_2S), 4.21 (1 H, m, 4-H), 4.32 (1 H, m, 5-H), and 7.15—7.45 (5 H, complex, aromatic); δ_C 15.39 (CH_3), 25.74 (CH_3), 28.46 (CH_3), 34.70 (CH_2), 73.63 (CH), 77.50 (CH), and aromatic resonances.

3-*Phenylthiotetrahydrofuran* (**45**).—To a stirred solution of a mixture of 1-phenylthiobutane-2,4-diol (**34**), 2-phenylthiobutane-1,4-diol (**35**) (0.21 g), and triphenylphosphine (0.26 g) in dry tetrahydrofuran (30 ml), diethyl azodiformate (0.17 g) in tetrahydrofuran (10 ml) was added dropwise under nitrogen at room temperature. After 10 h water (20 ml) was added and the mixture was extracted with ether (3 × 50 ml). The combined organic extracts were dried ($MgSO_4$), filtered, and evaporated under reduced pressure to afford after chromatography [eluant ethyl acetate–light petroleum (30:70)] as a colourless oil 3-*phenylthiotetrahydrofuran* (**45**) (140 mg, 74%) [Found: M^+, 180.0606 (51%). $C_{10}H_{12}OS$ requires M, 180.0605]; $\nu_{max.}$($CHCl_3$) 1 590 and 1 485 cm^{-1}; δ_H 1.88 (1 H, m) and 2.28 (1 H, m) (CH_2CH_2O), 3.60 (1 H, dd, J 9 and 5.5 Hz) and 4.07 (1 H, dd, J 9 and 6.5 Hz) (CH_2O), 3.7—3.95 (3 H, complex, CHS and CH_2O), and 7.15—7.4 (5 H, complex, aromatic); δ_C 33.26 (CH_2CH_2O), 44.88 (CHS), 67.53 (CH_2O), 73.58 (CH_2O), and 126.67, 128.97, 130.66, and 135.70 (aromatic carbon).

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