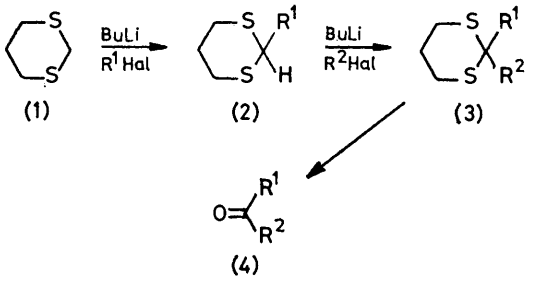
Acyl Anion Equivalents. Synthesis of Ketones and α-(Phenylthio)ketones from the Adducts of Bis(phenylthio)carbanions and Carbonyl Compounds [1]

By **Philip Blatcher** and **Stuart Warren,*** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

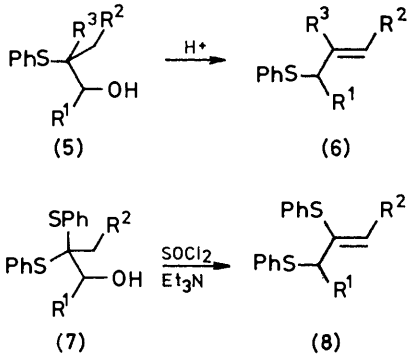
Bis(phenylthio)carbanions react with aldehydes and ketones to give α-hydroxybis(phenylthio)acetals. The aldehyde adducts give simple ketones with trifluoroacetic acid and α-(phenylthio)ketones with toluene-*p*-sulphonic acid. The effect of these reagents on the ketone adducts is also discussed. The mechanisms and scope of all the reactions are described. The synthesis of α-(phenylthio)ketones is regiospecific and makes these compounds available as specific enol equivalents.

THE limitations of carbonyl compounds as nucleophilic reagents in organic synthesis [2,3] have led to the development of reagents with umpolung [4,5] and specific enol equivalents [6] (enamines,[7] enol silanes,[8,9] *etc.*). Problems still arise with these reagents because they often give mixtures of products and equilibration between regioisomers can occur.[9] Corey and Seebach's solution to these problems has been to use dithioacetals,[10] especially dithians,[11] *e.g.* (1) and (2), to protect the carbonyl group against nucleophilic attack, and activate it for carbanion formation. This inevitably inverts the polarity [5,12] of the system as the anions from the dithians (1) and (2) are acyl anion equivalents.[13] In its simplest form [(1) ⟶ (4)] this gives a synthesis of ketones themselves.[14] There are problems here too: the second alkylation [(2) ⟶ (3)] does not always give good yields and it is sometimes difficult to remove the dithian [(3) ⟶ (4)] though there are now many methods for doing this.[11,14,15] Dithians have in general been more

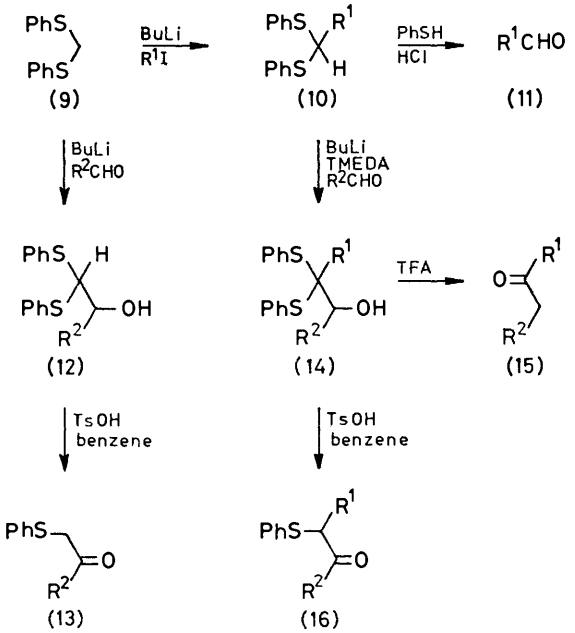


successful than other cyclic dithioacetals,[16] bis(arylthio)-acetals,[10,17-21] bis(alkylthio)acetals,[22] or their sulphoxides [23] offered as alternatives with special advantages, and have been used in the synthesis of molecules with complicated arrays of functional groups.[11,13,24]

We have been using phenylthio (PhS) migrations to synthesise allyl sulphides (6) by the acid-catalysed rearrangement of β-hydroxyalkyl phenyl sulphides [25] (5) and have therefore explored the chemistry of the α-hydroxybis(phenylthio)-compounds (7). Our aim was to rearrange these compounds to the bis-sulphides (8) which, being at once allyl and vinyl sulphides, should have an interesting chemistry. The reaction [(7) ⟶ (8)] does indeed take place in high yield with $SOCl_2$ and Et_3N but under the conditions we usually use for PhS migration [toluene-*p*-sulphonic acid (TsOH) in benzene under reflux or trifluoroacetic acid (TFA) at various temperatures] other reactions occurred which allowed us to develop the general syntheses of ketones and α-(phenylthio)ketones we now report.[1]



Preparation of α-Hydroxybis(phenylthio)acetals (14) *and* (19).—Bis(phenylthio)methane (9) (Scheme 1) is

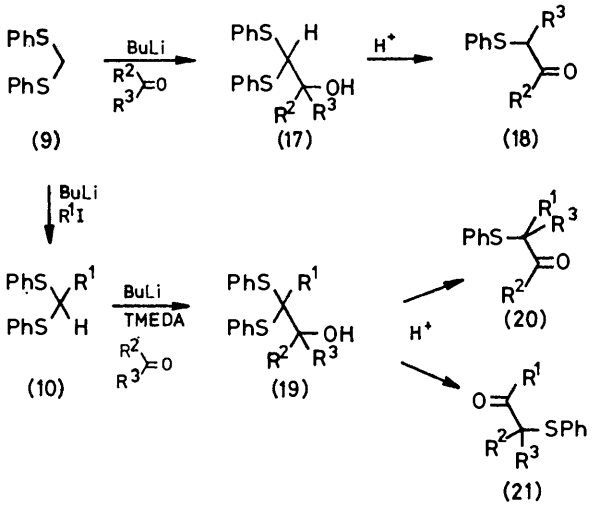


SCHEME 1 Adducts of bis(phenylthio)carbanions and aldehydes

readily available by displacement with benzenethiol on dihalogenomethanes.[10,26] It forms a yellow anion on

treatment with n-butyl-lithium (BuLi) in tetrahydrofuran (THF) which adds to aldehydes or ketones to give the adducts (12) or (17) in high yield (Table 2). Adducts of this type have been made previously.[10,17-21]

The alkylated compounds (10) can be made by treatment of the anion of (9) with an alkyl iodide (primary



SCHEME 2 Adducts of bis(phenylthio)carbanions and ketones

only) or directly from the aldehyde (11) with benzenethiol and HCl.[17,27] The second method is better for branched chain compounds (R^1 = sec-alkyl) and the only one for aromatic compounds (R^1 = Ar). It also gives quantitative yields from simple aldehydes (Table 1).

TABLE 1

Synthesis of bis(phenylthio)acetals (10)

R^1	Method [a]	Yield (%)
H	A	96
Me	B	99
Et	B	96
Pr^n	C	99
Pr^i	C	100
Bu^n	B	96
3-Methylbutyl	B	91
CH_2Ph	C	100
Ph	C	100

[a] A, Alkyl dihalide with PhS^-, see ref. 10. B, By alkylation of bis(phenylthio)methane carbanion. C, By R^1CHO + PhSH + HCl.

There are discouraging reports in the literature * on both the metallation of the alkylated compounds (10) and on the reaction of the resulting anions with carbonyl compounds. We have found that orange anions are formed by treatment with BuLi in THF in the presence of *NNN'N'*-tetramethylethylenediamine (TMEDA) for 15 min at 0 °C. Addition of an aldehyde or ketone instantly quenches the colour and gives good yields of adducts (14) and (19).

* Seebach (footnote 6 in *Synthesis*, 1969, 18) reports only 50% metallation of (10; R^1 = Et) with BuLi while Corey and Seebach originally reported (ref. 10) that metallation of these compounds (10) occurred only in the presence of diazabicyclo-octane (DABCO) and that even then the yield of adducts (14) with carbonyl compounds was only moderate. Other workers (refs. 17—21) also report low yields of adducts (14) and (19).

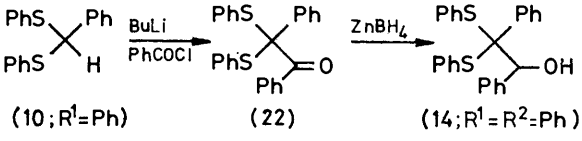
Benzaldehyde bis(phenylthio)acetal [18] (10; R^1 = Ph) gave a yellow anion on treatment with BuLi even in the absence of TMEDA but the anion did not react with aldehydes or ketones. It did react with benzoyl chloride to give the ketone (22) which was reduced to the alcohol (14; $R^1 = R^2$ = Ph) with *zinc* borohydride.[28] Sodium borohydride gave only the original acetal (10; R^1 = Ph).

TABLE 2

Adducts (14) and (19) of bis(phenylthio)carbanions with aldehydes and ketones

R^1	R^2	R^3	Yield of (14) or (19) (%)
H	Et	H	84
	Pr^i	H	86
	n-hexyl	H	79
	Me	*p*-Me-C_6H_4	86
	$[CH_2]_4$		76
Me	Me	H	52
	Et	H	84
	Pr^n	H	70
	Pr^n	D	67 [a]
	Ph	H	57
	Et	Et	76
Et	H	H	71
	Me	H	73
	Me	D	77 [a]
	Et	H	76
	n-hexyl	H	59
	Ph	H	89
	Ph	D	52
	Me	$PhCH_2$	56
	$[CH_2]_5$		68
Pr^n	Ph	Me	80
Pr^i	Ph	H	72
Bu^n	Me	H	62
3-methylbutyl	Me	Me	71
$PhCH_2$	Et	He	64
Ph	Ph	H	[b]

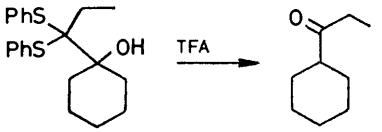
[a] Made from the undeuteriated alcohol by oxidation, and reduction ($NaBD_4$). This is the overall yield of the two steps. [b] Made by acylation (66%) and reduction (60%).



Synthesis of Ketones from α-Hydroxybis(phenylthio) Acetals (14).—When the aldehyde adducts (14) are dissolved in TFA at room temperature, reaction is instantaneous: an n.m.r. spectrum of the solution usually shows only diphenyl disulphide and the ketone (15). In some cases up to 10% of the α-(phenylthio)-ketone (16) is formed. The ketones (15) can be isolated in reasonable to excellent yields (Table 3) by evaporation and preparative t.l.c. No net rearrangement has occurred in the reaction: the original carbonyl group of the aldehyde (11) reappears and the α-hydroxy-group is replaced by hydrogen.

This is therefore a ketone synthesis with umpolung: [5,12] the anion from (10) is a masked acyl anion. It is also an alkylative 1,2-carbonyl transposition [29] on the aldehyde R^2CHO. The chief differences from the dithian route

to ketone [(1) ⟶ (4)] are that aldehydes are used instead of alkyl halides to introduce the second alkyl



(23) (24)

group (R^2CH_2) and that the products (15) are released from the adducts (14) under milder conditions than those needed for hydrolysis of dithians.

The reaction is limited almost entirely to aldehyde adducts (14) of substituted ($R^1 \neq H$) bis(phenylthio)-acetals (Table 3). The cyclohexanone adduct (23), alone among ketone adducts, gives a reasonable yield of the transposed ketone (24). Other ketone adducts (19) and adducts (12) or (17) of bis(phenylthio)methane with aldehydes or ketones give low yields of ketones or, more usually, α-(phenylthio)ketones with rearranged [(18) and (20)] carbon skeletons.

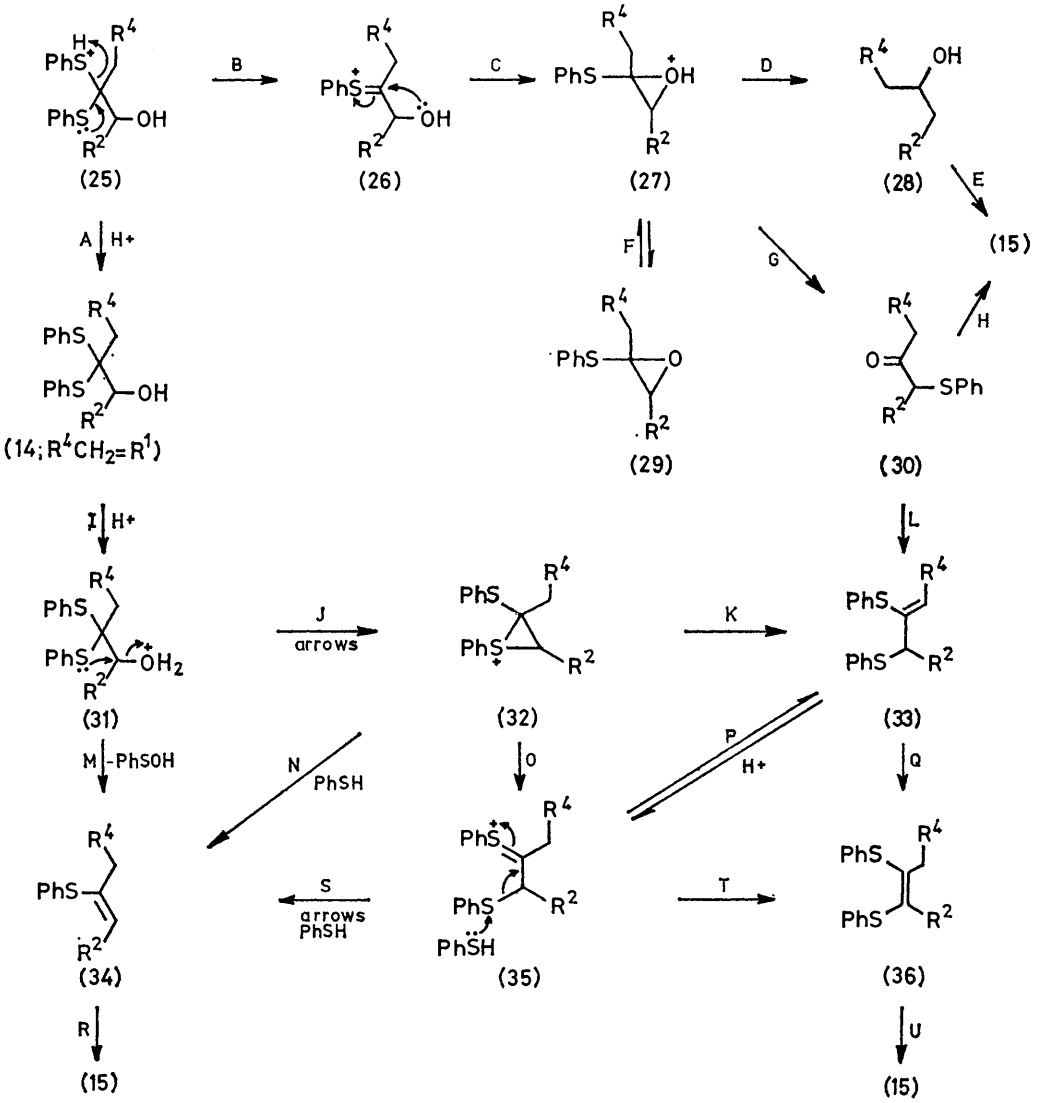
TABLE 3

Synthesis of ketones from aldehyde adducts (14)

Entry	R^1	R^2	Yield of (15) (%)
1	Me	Et	90 [a]
2	Me	Ph	87
3	Et	Me	90 [a]
4	Et	n-hexyl	31
5	Et	Ph	74
6	Pr^i	Ph	92
7	Bu^n	Me	80 [a]

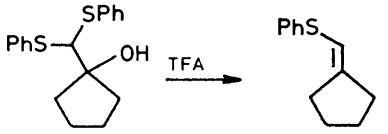
[a] By n.m.r.; other yields are of isolated product.

The many reasonable mechanisms for this intriguing reaction are summarised in Scheme 3. Protonation must occur initially at sulphur (Step A) or oxygen (Step I); thereafter most of the steps (C–U) are well established by precedent. Rearrangement (step G) of arylthio-



SCHEME 3 Mechanisms for the TFA reaction

epoxides (29) to α-(arylthio)ketones (30) has been reported.[30] The formation of compound (33) is our



(19; R^1 = H, R^2R^3 = $[CH_2]_4$)

$SOCl_2$–Et_3N reaction [see (7) ⟶ (8)]. Hydrolysis of vinyl sulphides (steps L and R) in TFA is a standard procedure.[1,31,32] Attack of benzenethiol on the PhS group of intermediates (32, step N), (35, step S), (27, step D), and (30, step H) is eminently reasonable and, since diphenyl disulphide is one of the products, must occur at some stage. Most of the other steps are additions or removals of protons.

Step M, the loss of PhSOH, may look odd at first but we have observed one such product, in low yield, in the reaction of the cyclopentanone adduct with TFA. The formation of PhSSPh from PhSOH and PhSH in acid solution would be expected.[33] The only intermediate we can definitely exclude is the bisvinyl sulphide (36) since entries 1 and 3 in Table 3 would both use the same intermediate (36), whereas in fact they give high yields of different ketones.

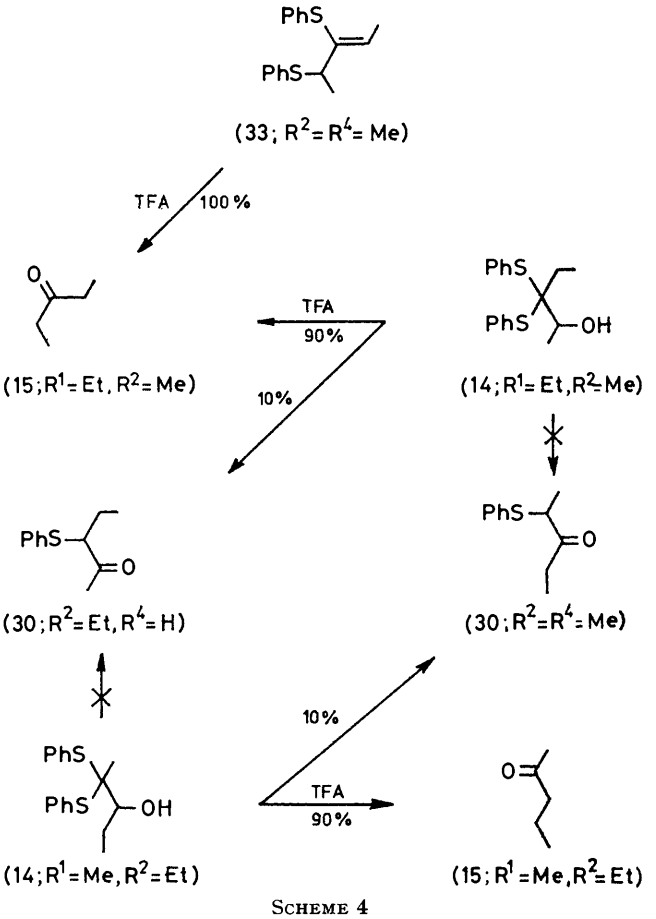
We were deterred from a mechanistic investigation into this reaction because (*a*) the reaction is instantaneous and we have been unable to measure its rate accurately, (*b*) in TFA diluted with other solvents (CCl_4, $CDCl_3$, and CD_3CN) or in other acidic media (HCO_2H, TsOH) other reactions occur, chiefly the formation of α-(phenylthio)ketones, and (*c*) attempts to compare the reaction (14) ⟶ (15) with the reactions of possible intermediates *e.g.* (30), with benzenethiol in TFA were thwarted by the low solubility of benzenethiol in TFA.

We have, however, tested the accessible intermediates under the reaction conditions. The rearranged compound (33) does give the ketone (15) at least as fast as it is formed from (14) itself. In addition, this is the cleanest of all the TFA reactions, giving only ketone (15) even when (14) does not (Scheme 4). The α-(phenylthio)-ketones (30) did not give the ketones (15) in TFA alone but did so when benzenethiol was added. The reaction appeared to be slower than (14) ⟶ (15) but that may be because benzenethiol is not very soluble in TFA. The best evidence against (30) as an intermediate came from the by-products of two reactions (Scheme 4). Each was formed in *ca.* 10% yield and each would be the intermediate in the formation of the other ketone. However, each survived the reaction conditions and cannot be an intermediate in the formation of the ketones (15).

It is certainly possible for either PhS or OH to act as the leaving group in TFA (steps A or I). The ketone adducts (17) and (18) react mostly by protonation and loss of PhS while the cyclic analogues (37) react by protonation and loss of OH under the same conditions.[34] We suggest that the evidence, such as it is, points to the route *via* a PhS migration (I, J, K, P, S, R). The key intermediate is therefore (35) and it is reasonable that it should be attacked at sulphur by PhSH to give (34) but at hydrogen by Et_3N to give (33).

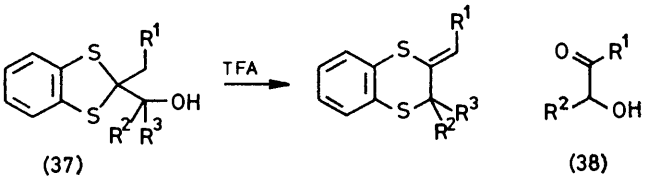
The amount of water present in the reaction mixture is obviously important. One mol is needed to form the ketones (15): one mol is provided by step J. There is in any case enough water in commercial TFA to hydrolyse a vinyl sulphide [31] or compound (33) to a ketone.

When we added more water to the reaction mixture the alcohols (14) were hydrolysed to α-hydroxyketones



SCHEME 4

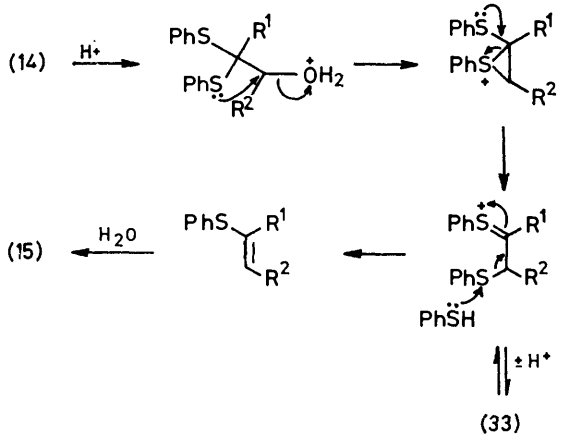
(38). However, on treatment of (33) with aqueous TFA the α-(phenylthio)ketone (30) did become a significant



(37) (38)

by-product (*ca.* 20%); cation (35) is being captured by water. Removal of water by treatment of (14) with TFA–TFA anhydride (1 : 1) gave (33) as a by-product. These results are consistent with the mechanism in Scheme 5.

Reactions of Ketone Adducts (19) *with TFA*.—The normal course of reaction is rearrangement of the carbon



SCHEME 5 Proposed mechanism for the TFA reaction

skeleton (40) after protonation and loss of PhS to give an α-(phenylthio)ketone (20) (Scheme 2 and Table 4). The reaction is unambiguous only if the ketone is symmetrical (entry 1, Table 4) or if one group, R^2 or R^3, migrates in

TABLE 4

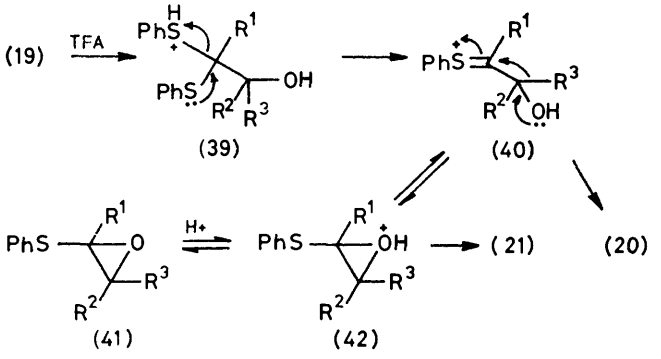
Reactions of ketone adducts (19) with TFA

Entry	R^1	R^2	R^3	Yield of product (20),[a] (%)
1	Me	Et	Et	50
2	H	Me	p-MeC_6H_4	52
3	Et	Me	CH_2Ph	91
4	Pr^n	Me	Ph	87

[a] R^3 migrates in each case; see Scheme 2.

preference to the other. Aryl groups (entries 2 and 4) or benzyl groups (entry 3) migrate in preference to methyl groups in this reaction.

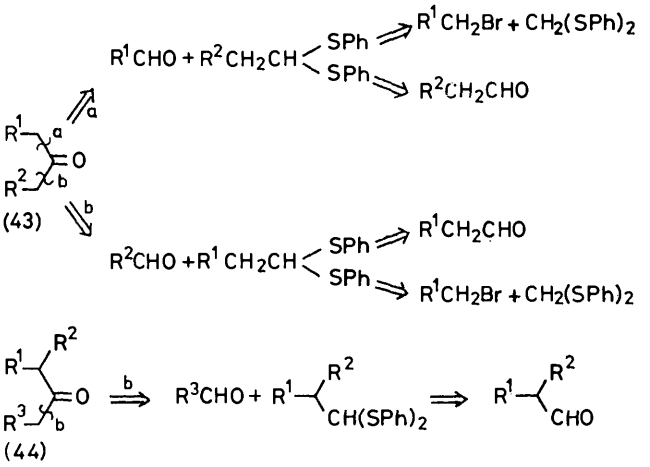
Cohen and his co-workers have reported [21] the same reaction in higher yield by specific removal of PhS with copper(I) trifluoromethanesulphonate. They observed migration of hydride and allyl groups and suggested that



the epoxides (41) were intermediates, though they also reported the more reasonable rearrangement of these same epoxides (41) by PhS migration to the isomeric α-(phenylthio)ketones (21). Since the epoxides must be formed from and decompose back to the same intermediates (40) and (42) on their way to (20), they are true intermediates not on this pathway but on the pathway to (21).

Retrosynthetic Analysis of the TFA Route to Ketones.—Ketones with two primary alkyl groups (43) may be made from four sets of starting materials (Scheme 6) since either disconnection (a) or (b) is acceptable. For ketones with one secondary alkyl group (44) disconnection (a) would mean using a ketone adduct and so (b) must be used. In this and in two of the alternatives for (43), the synthesis links two aldehydes by their carbonyl carbon atoms (Scheme 6).

Another approach, using in two cases similar compounds (14; R^1 = Bu, R^2 = n-C_5H_{11}) and (19; R^1 = Me, R^2R^3 = $[CH_2]_4$) has been reported by Mukaiyama *et al.*,[35] who treated the compounds with $TiCl_3$ and Et_3N followed by reduction with zinc to give vinyl sulphides which could be hydrolysed to ketones.



SCHEME 6 Retrosynthetic analysis of the ketone synthesis

Synthesis of α-(Phenylthio)ketones from α-Hydroxybis-(phenylthio)acetals (14) (*Table* 5).—Alcohols with one

TABLE 5

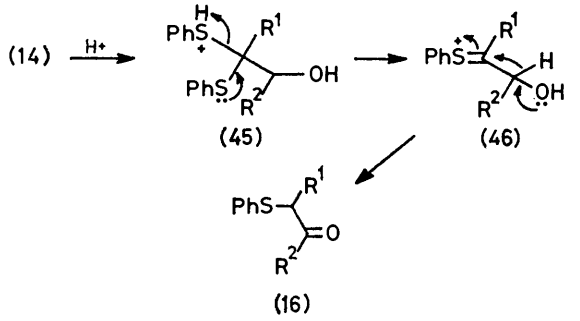
Synthesis of α-(phenylthio)ketones (16)

Entry	R^1	R^2	Yield of (16) (%)
1	H	Et	71
2		Pr^i	66
3		n-hexyl	61
4	Me	Me	82
5		Et	84
6		Pr^n	81
7		Ph	64[a]
8	Et	Me	80
9		Et	72
10		n-hexyl	58[a]
11	Bu^n	Me	78[a]

[a] Yield using 0.3 equiv. TsOH; others are with 1 equiv., which usually gives higher yield.

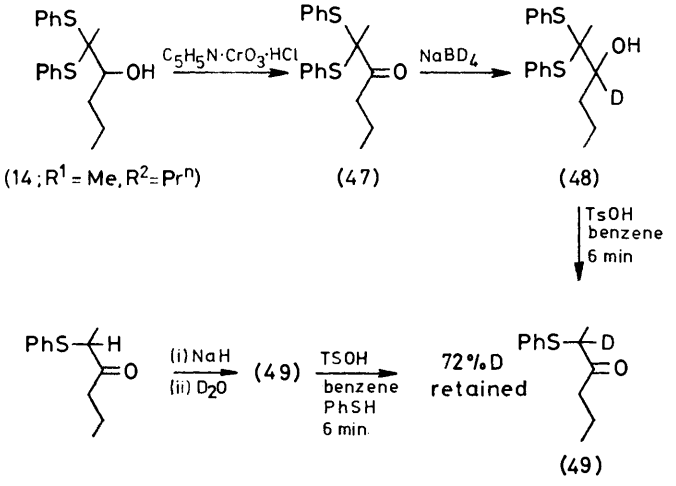
PhS [25] (5) or one diphenylphosphinoyl [36] (Ph_2PO) substituent rearrange on heating under reflux in benzene or toluene with TsOH catalyst. Under the same condi-

tions the aldehyde adducts (14) give α-(phenylthio)-ketones (16) without rearrangement. In contrast to



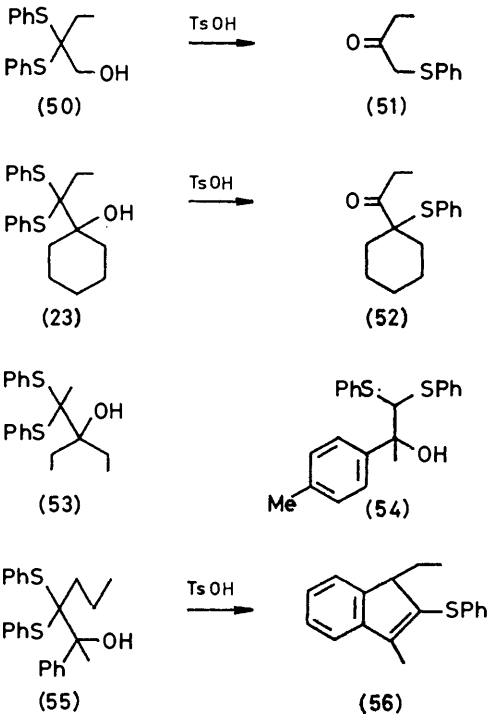
the synthesis of ketone (15), the carbonyl group of the second aldehyde (R^2CHO) is restored and that of the first aldehyde (R^1CHO, if used) is transposed. Though both sulphur and, preferentially no doubt, oxygen are protonated in this strong acid, the extra sulphur atom in (14) not present in (5) means that loss of PhSH (45) is preferred to loss of water. When the sulphur atom is attacked specifically with copper(I) trifluoromethanesulphonate, Cohen [21] observed the same reaction with one aldehyde adduct (14; R^1 = H, R^2 = Et). All his other reactions, and many of ours on the ketone adducts (19), are alkyl shifts, and since hydride migrates in preference to alkyl, even with a hydroxy-group at the migration origin,[37] it is reasonable to write the second step (46) as a hydride shift.

In fact, at least 40% of the reaction goes by a hydride



shift. The deuteriated alcohol (48), prepared *via* the ketone (47), gave an 85% yield of (49) with 38% deuterium at the marked position. This was measured by mass spectrometry both of the molecular ion and the fragment PhSCD·Me^+. It is a minimum value since a control experiment showed that the deuteriated product (49) lost *ca.* 30% of its deuterium under the reaction conditions. The rest of the reaction probably goes by simple elimination of PhSH.

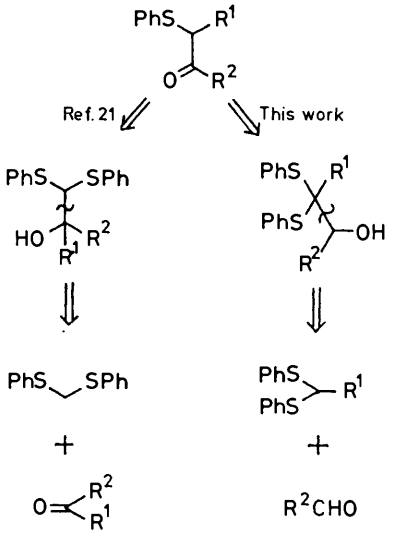
Scope and Retrosynthetic Analysis of the α-(Phenylthio)-ketone Synthesis.—The reaction is important because it provides a regiospecific synthesis of α-(phenylthio)-ketones. Previously, these have been made by sulphenylation of the parent ketone,[38] which is regioselective only if one side of the ketone is blocked or activated. Our synthesis is regiospecific because it is convergent. The carbon–carbon bond between the carbonyl group and the α-phenylthio-substituted atom is made in the first step so that formation of the alternative regioisomer is avoided. We can, for example, make both regioisomers of α-(phenylthio)hexan-3-one (entries 6 and 9, Table 5). The reaction works equally well on adducts of bis(phenylthio)methane (entries 1—3, Table 5) so that we can also prepare phenylthiomethyl ketones and the isomeric α-(phenylthio)alkyl ketones (*e.g.* entries 1 and 4, Table 5).



The scope of the reaction is quite large; R^1 [in (14)] can be H or primary alkyl, and R^2 can be primary or secondary alkyl or aryl. R^1 cannot be aryl but the product from the reaction would be (16; R^1 = Ar) which can be made by selective sulphenylation.[38] R^2 can be aryl only if R^1 is Me, otherwise a mixture of products is formed. R^2 cannot be hydrogen, but this would give α-(phenylthio)aldehydes which can be made from the corresponding nitriles [25] or esters.[31] We tried one case with R^2 = H (50); this gave 44% of the alternative α-(phenylthio)ketone (51). The cyclohexanone adduct (23) also gave this isomer (52) in 41% yield, but in general ketone adducts, *e.g.* (53) and (54) which give rearranged α-(phenylthio)ketones with TFA (Table 4), gave no recognisable products. One acetophenone adduct (55) gave a 57% yield of the 2-(phenylthio)indene (56).

Cohen's synthesis of an α-(phenylthio)ketone [21] is also

regiospecific and the retrosynthetic analyses of the two are compared in Scheme 7. Cohen's method is not



SCHEME 7 Retrosynthetic analysis of α-(phenylthio)ketone synthesis

convergent: it adds one carbon atom to another ketone and it requires that R^1 be a better migrating group than R^2. Our synthesis would be better for compounds such as entries 4—6, and 8—11 in Table 5 but Cohen's would be better for compounds (21) having the PhS group on a tertiary carbon atom. We can also make the same compounds by the TFA reaction on ketone adducts (Table 4).

This convergent synthesis of single isomers of α-(phenylthio)ketones gives them the status of specific enol equivalents since they form enolate ions in base only on the phenylthio side. We have already used them in this role in synthesis of butenolides and γ-phenylthio-acrylate esters.[39]

EXPERIMENTAL

General spectroscopic and chromatographic details have been given elsewhere.[31] Silica gel (Fison) was used for column chromatography. THF refers to tetrahydrofuran distilled from $LiAlH_4$ directly into the reaction vessel. TMEDA refers to *NNN'N'*-tetramethylethylenediamine distilled from CaH_2. 1,1-Bis(phenylthio)ethane was made by the method of Corey and Seebach.[10] N.m.r. signals marked with an asterisk belong to diastereotopic groups of protons.

Synthesis of Bis(phenylthio)acetals (10).—*1,1-Bis(phenylthio)propane* * (10; R^1 = Et). To a stirred solution of bis(phenylthio)methane [10] (4.64 g, 20 mmol) in dry THF (40 ml) at 0 °C under nitrogen was added n-butyl-lithium (1.54M-solution in hexane; 15 ml, 23 mmol). After 15 min, ethyl iodide (1.8 ml, 23 mmol) was added and the solution stirred at room temperature for one hour, poured into water (100 ml), extracted with ether (3 × 25 ml), the extract washed with water (2 × 20 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give an oil. Distillation gave the dithioacetal (4.97 g, 96%) as an oil, b.p. 126—130 °C at 0.1 mmHg (lit.,[40] 150—155 °C at 0.1 mmHg), δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 × SPh), 4.34 (1 H, t, *J* 6 Hz, C*H*CH_2), 1.88 (2 H, quintet, *J* 6 Hz, CHCH_2Me), and 1.11 (3 H, t, *J* 6 Hz, CH_2*Me*).

1,1-Bis(phenylthio)butane [42] (10; R^1 = Pr^n). Hydrogen chloride was bubbled through a stirred ice-cooled solution of butyraldehyde (3.6 g, 4.43 ml, 50 mmol) in benzenethiol (35 ml, 340 mmol) for 1 h. The mixture was stirred for a further 2 h as it warmed up to room temperature. Ether (200 ml) was then added, the solution washed with 10% sodium hydroxide (3 × 50 ml), water (2 × 50 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give an oil. Distillation gave the dithioacetal (12.85 g, 99%) as an oil, b.p. 145—155 °C at 0.1 mmHg, $\nu_{max.}$ (liq) 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.6—7.1 (10 H, m, Ph), 4.39 [1 H, t, *J* 6.5 Hz, $CH_2CH(SPh)_2$], 2.0—1.4 (4 H, m, CH_2CH_2), and 0.86 (3 H, t, *J* 7 Hz, Me), *m/e* 274 (M^+, 46%), 197 (*M* − Ph, 65), 165 (*M* − SPh, 36), 123 ($PhSCH_2$, 100), and 110 (PhSH, 97) (Found: C, 70.1; H, 6.5; S, 23.1. $C_{16}H_{18}S_2$ requires C, 70.0; H, 6.61; S, 23.4%).

2-Methyl-1,1-bis(phenylthio)propane † (10, R^1 = Pr^i). Prepared as for 1,1-bis(phenylthio)butane but using isobutyraldehyde (1.75 g, 2.2 ml, 24 mmol) and benzenethiol (23.4 g, 214 mmol), the dithioacetal (6.9 g, 100%) was an oil, $\nu_{max.}$ (liq) 1 585 cm^{-1} (PhS), δ($CDCl_3$) 7.50—7.14 (10 H, m, 2 SPh), 4.40 [1 H, d, *J* 3.5 Hz, C*H*$(SPh)_2$], 2.20 (1 H, sept of d, *J* 3.5 and 6.5 Hz, C*H*Me_2), and 1.14 (6 H, d, *J* 6.5 Hz, CHMe_2), *m/e* 274 (M^+, 62%), 231 (*M* − Pr^i, 6), 165 (*M* − PhS, 100), and 110 (PhSH, 28) (Found: C, 70.2; H, 6.65; S, 23.6. $C_{16}H_{18}S_2$ requires C, 70.0; H, 6.61; S, 23.4%).

1,1-Bis(phenylthio)pentane ‡ (10, R^1 = Bu^n). Preparation as for 1,1-bis(phenylthio)propane but using n-butyl iodide (3.68 g, 2.28 ml, 20 mmol) instead of ethyl iodide gave an oil. Distillation gave the dithioacetal (5.5 g, 96%), b.p. 150—160 °C at 0.05—0.1 mmHg, $\nu_{max.}$ (liq) 1 582 cm^{-1} (PhS), δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 × SPh), 4.45 (1 H, t, *J* 6 Hz, PhSC*H*CH_2), 2.2—1.1 (6 H, m, $[CH_2]_3$), and 0.92 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 288 (M^+, 25%), 179 (*M* − SPh, 100), and 110 (PhSH, 47) (Found: C, 70.5; H, 7.1; S, 22.0. $C_{17}H_{20}S_2$ requires C, 70.8; H, 6.98; S, 22.2%).

4-Methyl-1,1-bis(phenylthio)pentane (10; R^1 = *3-methylbutyl*). Preparation as for 1,1-bis(phenylthio)propane but using isoamyl iodide (2.62 ml, 3.95 g, 20 mmol) instead of methyl iodide gave an oil (6.44 g). This was purified by column chromatography (50-fold excess of silica gel; acetone–petroleum ether, b.p. 60—80 °C, 1 : 4) to give the *dithioacetal* (5.54 g, 91%) as an oil, R_F (acetone–light petrol 1 : 4) 0.58, $\nu_{max.}$ (liq) 1 574 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.1 (10 H, m, 2 × SPh), 4.41 [1 H, t, *J* 7 Hz, C*H*$(SPh)_2$], 2.1—1.70 [2 H, m, $(PhS)_2CHCH_2$], 1.70—1.30 (3 H, m, $CH_2CH$$Me_2$), and 0.87 (6 H, d, *J* 7.5 Hz, CHMe_2), *m/e* 302 (M^+, 7%), 193 (*M* − SPh, 100), and 110 (PhSH, 78) (Found: C, 71.5; H, 7.4; S, 20.9. $C_{18}H_{22}S_2$ requires C, 71.5; H, 7.33; S, 21.2%).

2-Phenyl-1,1-bis(phenylthio)ethane (10; R^1 = CH_2Ph). Prepared as for 1,1-bis(phenylthio)butane but using phenylacetaldehyde (2.4 g, 20 mmol) and benzenethiol (20 ml, 180 mmol), the *dithioacetal* (6.5 g, 100%) was an oil, R_F (CCl_4) 0.30, $\nu_{max.}$ (liq) 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.5—7.0 (15 H, m, 3 × Ph), 4.43 [1 H, t, *J* 7 Hz, $CH_2CH(SPh)_2$], and 3.08 (2 H, d, *J* 7 Hz, CH_2CH), *m/e* 322 (M^+, 1%),

* This compound has been prepared by others [40,41] but full details have not been published.

† This compound has been prepared by others [41] but full details have not yet appeared.

‡ Prepared by the same method, but not characterised, see ref. 10.

213 (M − PhS, 20), 123 ($PhSCH_2$, 38), 109 (PhS, 100), 91 ($PhCH_2$, 28), and 77 (Ph, 34) (Found: M^+, 322.085 1. $C_{20}H_{18}S_2$ requires M, 322.085 1).

1-*Phenylbis(phenylthio)methane* (10; R^1 = Ph). Prepared as for 1,1-bis(phenylthio)butane but using benzaldehyde (2.2 g, 20 mmol) and benzenethiol (20 ml, 194 mmol), the dithioacetal was an oil. Crystallisation from n-pentane gave the dithioacetal (6.2 g, 100%) as needles, m.p. 50—51 °C (lit.,[18] 52—53 °C), $\nu_{max.}$ (liq) 1 581 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.0 (15 H, m, 3 × Ph) and 5.45 (1 H, s, PhC*H*).

Synthesis of α-Hydroxy-dithioacetals (14 *and* 19).—1,1-*Bis(phenylthio)butan-2-ol* (14; R^1 = H, R^2 = Et). *Method A*. n-Butyl-lithium (1.6M-solution in hexane; 2.6 ml, 4.15 mmol) was added to a stirred solution of bis(phenylthio)methane (0.93 g, 4 mmol) in dry THF (20 ml) under nitrogen at 0 °C. After 10 min, the yellow anion was quenched by dropwise addition of propionaldehyde (0.23 g, 0.29 ml, 4 mmol). The ice-bath was then removed and the solution stirred for 30 min, poured into water (50 ml), and extracted with ether (3 × 25 ml). The extract was washed with water (3 × 25 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give an oil, which was purified by preparative t.l.c. to give the *alcohol* (0.97 g, 84%) as an oil, R_F (CH_2Cl_2) 0.38, $\nu_{max.}$ (liq) 3 440br (OH), 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.0 (10 H, m, 2 × SPh), 4.47 (1 H, d, *J* 4 Hz, PhSC*H*–CH), 3.9—3.5 (1 H, m, C*H*OH, simplified on shaking with D_2O), 2.81 (1 H, d, *J* 3 Hz, CH–O*H*, removed by D_2O), 2.1—1.4 (2 H, m, CH_2*Me), and 0.95 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 290 (M^+, 10%), 231 (M − EtCHOH, 9.5), 181 (M − SPh, 100), and 109 (PhS, 28) (Found: C, 66.4; H, 6.25; S, 21.8. $C_{16}H_{18}OS_2$ requires C, 66.2; H, 6.24; S, 22.1%).

3-*Methyl*-1,1-*bis(phenylthio)butan-2-ol* (14; R^1 = H, R^2 = Pr^i). n-Butyl-lithium (1.6M in hexane; 2.7 ml, 4.3 mmol), bis(phenylthio)methane (0.93 g, 4 mmol), and isobutyraldehyde (0.38 ml, 4.5 mmol) (method A) gave the *alcohol* (1.04 g, 86%) as an oil, R_F ($CHCl_2$) 0.50, $\nu_{max.}$ (liq) 3 490br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.0 (10 H, m, 2 × SPh), 4.56 (1 H, d, *J* 4 Hz, HOCHC*H*SPh), 3.44 [1 H, dt, *J* 4 and 7 Hz, CHC*H*(OH)CH], 2.91 (1 H, d, *J* 4 Hz, CHO*H*, removed by D_2O), 2.23 (1 H, octet, *J* 7 Hz, Me_2CHCH), and 1.00 and 0.88 (each 3 H, d, *J* 7 Hz, CHCH*-*Me_2), *m/e* 304 (M^+, 2%), 194 (M − PhSH, 55), 123 (PhS–CH_2, 100), and 110 (PhSH, 96) (Found: M^+, 304.095 5. $C_{17}H_{20}OS_2$ requires M, 304.095 5).

1,1-*Bis(phenylthio)octan-2-ol* (14; R^1 = H, R^2 = n-hexyl). n-Butyl-lithium (1.6M in hexane; 2.7 ml, 4.3 mmol), bis(phenylthio)methane (0.93 g, 4 mmol), and n-heptanal (0.58 ml, 4.3 mmol) (method A) gave the *alcohol* (0.74 g, 79% based on recovered starting material) as an oil, R_F (CH_2Cl_2) 0.50, $\nu_{max.}$ (liq) 3 440br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.1 (10 H, m, 2 × SPh), 4.47 [1 H, d, *J* 4 Hz, CHC*H*$(SPh)_2$], 3.82 (1 H, dt, *J* 4, 7 Hz, CHC*H*CH*$_2$), 2.76 (1 H, s, OH, removed by D_2O), 2.1—1.1 (10 H, m, 5 × CH_2), 0.88 (3 H, distorted t, Me), *m/e* 346 (M^+, 9%), 337 (M − SPh, 100), 231 (PhSCHSPh, 20), and 110 (PhSH, 26) (Found: M^+, 346.144 6. $C_{20}H_{26}OS_2$ requires M, 346.142 4).

2-(4-*Methylphenyl*)-1,1-*bis(phenylthio)propan-2-ol* (19; R^1 = H, R^2 = Me, R^3 = *p*-MeC_6H_4). n-Butyl-lithium (2.37M in hexane; 2.3 ml, 5.5 mmol), bis(phenylthio)-methane (1.16 g, 5 mmol) and 4-methylacetophenone (0.67 g, 0.66 ml, 5 mmol) (method A) gave the *alcohol* (1.57 g, 86%) as an oil, R_F (CH_2Cl_2) 0.52, $\nu_{max.}$ (liq) 3 495br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.46—6.96 (14 H, m, 2 × S*Ph* and C_6H_4Me), 4.65 (1 H, s, PhSC*H*), 3.16 (1 H, s, OH, removed by D_2O), 2.29 (3 H, s, C_6H_4*Me*), and 1.79 (3 H, s, *Me*COH), *m/e* 257 (M − SPh, 39%), 232 ($PhSCH_2SPh$, 98), 134 (60), 43 (100) [Found: M − SPh, 257.098 3. $C_{16}H_{17}OS$ requires 257.099 9. Found: $PhSCH_2SPh$, 232.038 3. $C_{13}H_{12}S_2$ requires 232.038 0. Found: M − $(PhS)_2CH$, 135.081 1. $C_9H_{11}O$ requires 135.080 9].

1-[*Bis(phenylthio)methyl*]*cyclopentanol* * (19; R^1 = H, R^2-R^3 = $[CH_2]_4$). n-Butyl-lithium (2.4M in hexane; 2.3 ml, 5.5 mmol), bis(phenylthio)methane (1.16 g, 5 mmol), and cyclopentanone (0.42 g, 0.45 ml, 5 mmol) (method A) gave an oil. Crystallisation from light petroleum (b.p. 60—80 °C) gave the alcohol (1.2 g, 76%), m.p. 37—38 °C, R_F (CH_2Cl_2) 0.41, $\nu_{max.}$ ($CHCl_3$) 3 540br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.43—7.1 (10 H, m, 2 × SPh), 4.56 (1 H, s, PhSC*H*), 2.55 (1 H, s, OH, removed by D_2O), and 1.86 (8 H, m, cyclopentyl), *m/e* 316 (M^+, 9%), 232 ($PhSCH_2SPh$, 15), 207 (M − SPh, 100), and 110 (PhSH, 94) (Found: C, 68.1; H, 6.35; S, 20.4. $C_{28}H_{20}OS_2$ C, 68.3; H, 6.37; S, 20.3%).

3,3-*Bis(phenylthio)butan-2-ol* † (14, R^1 = R^2 = Me). *Method B*. n-Butyl-lithium (2.8M-solution in hexane; 1.0 ml, 2.8 mmol) was added to a stirred solution of 1,1-bis(phenylthio)ethane (0.62 g, 2.5 mmol) in dry THF (15 ml) and TMEDA (0.39 ml, 2.7 mmol) under nitrogen at 0 °C. After 10 min, dry lithium bromide (0.5 g) in dry THF (5 ml) was added followed by acetaldehyde to discharge the orange colour due to the anion. Further n-butyl-lithium (0.2 ml) was then added and the orange colour discharged again with acetaldehyde; this procedure was repeated once more. The ice-bath was then removed and the solution stirred for 30 min and worked up as in method A to give the *alcohol* (0.38 g, 52%) as an oil, R_F (CH_2Cl_2) 0.37, $\nu_{max.}$ (liq) 3 490br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 × SPh), 3.77 (1 H, q, *J* 6 Hz, C*H*Me), 2.98 (1 H, s, OH, removed by D_2O), 1.37 (3 H, d, *J* 6 Hz, CH*Me*), and 1.19 (3 H, s, PhSC*Me*), *m/e* 245 (M − MeCHOH, 5%), 181 (M − PhS, 73), 137 (PhSCHMe, 99), and 110 (PhSH, 100) (Found: C, 66.3; H, 6.5; S, 21.9. $C_{16}H_{18}OS_2$ requires C, 66.2; H, 6.24; S, 22.1%).

2,2-*Bis(phenylthio)pentan-3-ol* (14; R^1 = Me, R^2 = Et). *Method C*. n-Butyl-lithium (1.5M-solution in hexane; 1.3 ml, 2 mmol) was added to a stirred solution of 1,1-bis(phenylthio)ethane (460 mg, 1.86 mmol) in dry THF (15 ml) and TMEDA (0.3 ml, 2.1 mmol) under nitrogen at 0 °C. After 15 min propionaldehyde was added dropwise to discharge the orange colour of the anion. Further n-butyl-lithium (0.3 ml) was then added and the orange colour again discharged with propionaldehyde; this procedure was repeated once more. The ice-bath was then removed and the solution stirred for 30 min and worked up as in method A to give the *alcohol* (477 mg, 84%) as an oil, R_F (CH_2Cl_2) 0.51, $\nu_{max.}$ (liq) 3 475br (OH) and 1 579 cm^{-1} (PhS), δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 × SPh), 3.47 (1 H, dd, *J* 3, 9 Hz, CH*$_2$C*H*OH), 3.16 (1 H, s, OH, removed by D_2O), 2.1—1.4 (2 H, m, CH_2), 1.25 (3 H, s, PhSCMe), and 1.05 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 304 (M^+, 2%), 245 (M − EtCHOH, 6), 185, (M − SPh, 100), and 110 (PhSH, 38) (Found: C, 66.8; H, 6.9; S, 21.2. $C_{17}H_{20}OS_2$ requires C, 67.0; H, 6.62; S, 21.1%).

* This compound has been prepared by others [21] but full details have not yet been published.

† A total of 3 additions of n-butyl-lithium and carbonyl compound were made in the preparation of all α-hydroxydithioacetals (14 and 19; $R^1 \neq$ H) unless otherwise stated.

2,2-*Bis*(*phenylthio*)*hexan*-3-*ol* (14; R^1 = Me, R^2 = Pr^n). 1,1-Bis(phenylthio)ethane (493 mg, 2 mmol), TMEDA (0.35 ml, 2.5 mmol), n-butyl-lithium (1.5M in hexane; 1.9 ml, 2.85 mmol), and n-butyraldehyde (method C) gave the *alcohol* (445 mg, 70%) as an oil, R_F (CH_2Cl_2) 0.59, $\nu_{max.}$ (liq) 3 470br (OH) and 1 578 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.1 (10 H, m, 2 × SPh), 3.55 (1 H, dd, *J* 3 and 8 Hz, CH_2*-C*H*OH), 3.04 (1 H, s, OH), 2.0—1.1 (4 H, m, 2 × CH_2), 1.23 (3 H, s, PhSC*Me*), and 0.92 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 209 (*M* − SPh, 52%), 166 (*M* − Ph − SPr^n, 44), and 110 (PhSH, 100) (Found: *M* − PhS, 209.099 5. $C_{12}H_{17}OS$ requires 209.099 9. Found: *M* − Ph − SPr^n, 166.045 1. $C_9H_{10}OS$ requires 166.045 2. Found: C, 68.0; H, 6.8. $C_{18}H_{22}OS_2$ requires C, 67.9, H, 6.92%).

2,2-*Bis*(*phenylthio*)*hexan*-3-*one* (47). To a mixture of pyridinium chlorochromate [43] (280 mg, 1.4 mmol) and sodium acetate (18 mg, 0.23 mmol), stirred at room temperature in dry dichloromethane (1.5 ml), was added the alcohol (14; R^1 = Me, R_3 = Pr^n) (222 mg, 0.7 mmol) in dichloromethane (1.5 ml). After 23 and 34 h additional chlorochromate (2 × 90 mg) was added and after 53 h ether (10 ml) was added and the solution decanted from the black residue. The residue was washed with more ether (3 × 5 ml), the ether solution filtered through Hyflosupercel, dried ($MgSO_4$), and evaporated *in vacuo* to give the *bis*-(α-*phenylthio*)*ketone* (147 mg, 67%) as a yellow oil, R_F (CH_2Cl_2) 0.74, $\nu_{max.}$ (liq) 1 700 (C=O) and 1 577 cm^{-1} (PhS), δ($CDCl_3$) 7.8—6.9 (10 H, m, 2 × SPh), 2.96 (2 H, t, *J* 7 Hz, CH_2CH_2CO), 1.69 (2 H, sext, *J* 7 Hz, CH_2CH_2Me), 1.40 (3 H, s, *Me*CSPh), and 0.99 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 316 (M^+, 1%), 245 (*M* − Pr^nCO, 100), 207 (*M* − SPh, 82), 109 (PhS, 26), and 71 (Pr^nCO, 13) (Found: M^+, 316.096 0. $C_{18}H_{20}OS_2$ requires 316.095 6).

2,2-*Bis*(*phenylthio*)-[3-^{2}H]*hexan*-3-*ol* (48 *or* 19; R^1 = Me, R^2 = Pr^n, R^3 = ^{2}H). Sodium borodeuteride (20 mg, 0.5 mmol) was added to a stirred solution of 2,2-bis(phenylthio)-hexan-3-one (142 mg, 0.45 mmol) in ethanol (5 ml) and the mixture stirred at room temperature for 6 h. After evaporation *in vacuo*, saturated ammonium chloride (10 ml) was added and the mixture extracted with chloroform (1 × 10 ml, 2 × 5 ml). The extract was washed with water (5 ml), dried ($MgSO_4$), and evaporated to give the *alcohol* (144 mg, 100%) as an oil, R_F (CH_2Cl_2) 0.52, $\nu_{max.}$ (liq) 2 460br (OH) and 1 577 cm^{-1} (PhS), δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 × SPh), 2.78 (1 H, s, OH, removed by D_2O), 2.0—1.1 (4 H, m, CH_2CH_2), 1.21 (3 H, s, PhSC*Me*), and 0.94 (3 H, t, *J* 6 Hz, CH_2*Me*), *m/e* 319 (M^+, 0.1%), 245 (*M* − Pr^nCDOH, 3), 210 (*M* − SPh, 42), 167 (*M* − SPh − Pr^n, 27), and 110 (PhSH, 100) (Found: *M* − Pr^nCDOH, 245.045 1. $C_{14}H_{13}S_2$ requires 245.045 9. Found: *M* − SPh, 210.105 6. $C_{12}H_{16}DOS$ requires 210.106 5).

1-*Phenyl*-2,2-*bis*(*phenylthio*)*propan*-1-*ol* (14; R^1 = Me, R^2 = Ph). 1,1-Bis(phenylthio)ethane (0.62 g, 2.5 mmol), TMEDA (0.31 g, 2.7 mmol), n-butyl-lithium (1.54M in hexane; 1.9 ml, 2.9 mmol), and benzaldehyde (0.27 g, 2.5 mmol) (method C; only one addition of butyl-lithium) gave, on evaporation of the extracts, a yellow solid. Recrystallisation from light petroleum (b.p. 60—80 °C) gave the *alcohol* (0.5 g, 57%), m.p. 137—138 °C, R_F (CH_2Cl_2) 0.53, $\nu_{max.}$ ($CHCl_3$) 3 480br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.6—7.2 (15 H, m, 2 × PhS and Ph), 4.70 (1 H, d, *J* 2 Hz, PhC*H*OH, collapses to s with D_2O), 3.62 (1 H, d, *J* 2 Hz, PhCHO*H*, removed by D_2O), and 1.13 (3 H, s, Me), *m/e* 352 (M^+, 1.4%), 245 (*M* − PhCHOH, 100), 243 (*M* − PhS, 100), and 110 (PhSH, 100) (Found: C, 71.3; H, 5.75; S, 18.4. $C_{21}H_{20}OS_2$ requires C, 71.6; H, 5.72; S, 18.2%).

3-*Ethyl*-2,2-*bis*(*phenylthio*)*pentan*-3-*ol* (19; R^1 = Me, R^2 = R^3 = Et). 1,1-Bis(phenylthio)ethane (1.23 g, 5 mmol), TMEDA (0.64 g, 0.78 ml, 5.4 mmol), n-butyl-lithium (2.8M in hexane 2.0 ml), and pentan-3-one (method C) gave the *alcohol* (1.25 g, 76%) as an oil, R_F (CH_2Cl_2) 0.55, $\nu_{max.}$ (liq) 2 490br (OH) and 1 579 cm^{-1} (PhS), δ($CDCl_3$) 7.6—7.1 (10 H, m, 2 × SPh), 2.66 (1 H, s, OH, removed by D_2O), 1.92 (4 H, q, *J* 8 Hz, 2 × CH_2Me), 1.22 (3 H, s, PhSC*Me*), and 1.05 (6 H, t, *J* 8 Hz, 2 × CH_2*Me*), *m/e* 222 (*M* − PhS, 100%), 193 (*M* − PhS − Et, 93), 135 (PhS−C=CH_2, 84), and 110 (PhSH, 93) (Found: C, 68.2; H, 7.3; S, 19.3. $C_{19}H_{24}OS_2$ requires C, 68.6; H, 7.28; S, 19.3%).

2,2-*Bis*(*phenylthio*)*butan*-1-*ol* (14; R^1 = Et, R^2 = H). 1,1-Bis(phenylthio)propane (390 mg, 1.5 mmol), TMEDA (0.3 ml, 2.1 mmol), n-butyl-lithium (1.7M in hexane; 1 ml), and paraformaldehyde (75 mg, added under a rapid stream of N_2) (method C, only 1 addition of n-butyl-lithium) gave the *alcohol* (307 mg, 71%) as an oil, R_F (CH_2Cl_2) 0.35, $\nu_{max.}$ (liq) 3 450br (OH) and 1 577 cm^{-1} (PhS), δ($CDCl_3$) 7.8—7.1 (10 H, m, 2 × SPh), 3.50 (2 H, s, CH_2OH), 2.62 (1 H, s, OH, removed by D_2O), 1.68 (2 H, q, *J* 7 Hz, CH_2Me), and 1.11 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 181 (*M* − SPh, 74%), 151 (*M* − SPh − C_2H_6, 26), 110 (PhSH, 100), and 71 (*M* − SPh − PhSH, 47) (Found: C, 66.0; H, 6.45; S, 22.3. $C_{16}H_{18}OS_2$ requires C, 66.2; H, 6.24; S, 22.1%).

3,3-*Bis*(*phenylthio*)*pentan*-2-*ol* (14; R^1 = Et, R^2 = Me). 1,1-Bis(phenylthio)propane (1.3 g, 5 mmol), TMEDA (0.8 ml, 5.6 mmol), n-butyl-lithium (2.5M in hexane; 2.2 ml, 5.5 mmol), lithium bromide (1 g), and acetaldehyde (method B) gave the *alcohol* (1.11 g, 73%) as an oil, R_F (CH_2Cl_2) 0.40, $\nu_{max.}$ (liq) 3 460br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.1 (10 H, m, 2 × SPh), 3.90 (1 H, quint, *J* 6 Hz, MeC*H*OH, collapses to q with D_2O), 2.55 (1 H, d, *J* 6 Hz, CHO*H*, removed by D_2O), 2.0—1.2 (2 H, m, CH_2Me), 1.40 (3 H, d, *J* 6 Hz, CH*Me*), and 1.06 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 304 (M^+, 1%), 259 (*M* − Et, 18), 195 (*M* − SPh, 100), and 110 (PhSH, 100) (Found: C, 67.0; H, 6.8; S, 20.8. $C_{17}H_{20}OS_2$ requires C, 67.0; H, 6.62; S, 21.1%).

3,3-*Bis*(*phenylthio*)*pentan*-2-*one*. Prepared in the same way as (47) from the alcohol (14; R^1 = Et, R^2 = Me) (150 mg), the crude product was purified by preparative t.l.c. (CH_2Cl_2) to give the *bis*-(α-*phenylthio*)*ketone* (122 mg, 82%) as an oil, R_F (CH_2Cl_2) 0.65, $\nu_{max.}$ (liq) 1 697 (C=O) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.6—7.1 (10 H, m, 2 × SPh), 2.42 (3 H, s, MeCO), 1.70 (2 H, q, *J* 7 Hz, CH_2Me), and 0.995 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 302 (M^+, 3%), 259 (*M* − MeCO, 41), 193 (*M* − PhS, 95), 109 (PhS, 19), and 43 (MeCO, 100) (Found: M^+, 302.078 6. $C_{17}H_{18}OS_2$ requires *M*, 302.079 9).

3,3-*Bis*(*phenylthio*)-[2-^{2}H]*pentan*-2-*ol* (19; R^1 = Et, R^2 = Me, R^3 = ^{2}H). Prepared as before by reduction of 3,3-bis(phenylthio)pentan-2-one (105 mg), the *alcohol* (99 mg, 94%) was an oil, R_F (CH_2Cl_2) 0.38, $\nu_{max.}$ (liq) 3 460br (OH) and 1 579 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.1 (10 H, m, 2 × SPh), 2.44 (1 H, OH, s, removed by D_2O), 1.9—1.3 (2 H, m, CH_2Me), 1.35 (3 H, s, *Me*CDOH), 1.01 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 305 (M^+, 0.4%), 259 (*M* − MeCDOH, 7), 196 (*M* − PhS, 100), and 110 (PhSH, 28) (Found: M^+, 305.101 1. $C_{17}H_{19}DOS_2$ requires *M*, 305.101 8).

4,4-*Bis*(*phenylthio*)*hexan*-3-*ol* (14; R^1 = R^2 = Et). 1,1-Bis(phenylthio)propane (1.3 g, 5 mmol), TMEDA (0.64 g, 0.78 ml, 5.4 mmol), n-butyl-lithium (2.8M in hexane;

2 ml, 5.4 mmol) and propionaldehyde (method C) gave the *alcohol* (1.21 g, 76%) as an oil, R_F (CH_2Cl_2) 0.53, $\nu_{max.}$ (liq) 3 485br (OH) and 1 581 cm^{-1} (PhS), δ($CDCl_3$) 7.8—7.0 (10 H, m, 2 × SPh), 3.58 (1 H, dd, *J* 3 and 8 Hz, CH_2CHOH), 2.42 (1 H, s, OH, removed by D_2O), 2.0—1.3 (4 H, m, 2 × CH_2), and 1.0 (6 H, t, *J* 8 Hz, 2 × Me), *m/e* 318 (M^+, 1%), 259 (*M* − EtCHOH, 8), 209 (*M* − SPh, 100), 109 (PhS, 45), and 56 (94) (Found: M^+, 318.111 9. $C_{18}H_{22}OS_2$ requires *M*, 318.111 1).

3,3-*Bis*(*phenylthio*)*decan*-4-*ol* (14; R^1 = Et, R^2 = n-hexyl). 1,1-Bis(phenylthio)propane (0.65 g, 2.5 mmol), TMEDA (0.39 ml, 2.7 mmol), n-butyl-lithium (2.8M in hexane; 1 ml), and n-heptanal (method C) gave the *alcohol* (0.55 g, 59%) as an oil, R_F (CH_2Cl_2) 0.64, $\nu_{max.}$ (liq) 3 480br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.8—7.18 (10 H, m, 2 × SPh), 3.78—3.58 (1 H, m, HOC*H*CH*$_2$), 2.39 (1 H, s, OH, removed by D_2O), and 2.0—0.76 (18 H, m, Et and [CH_2]$_5$*Me*), *m/e* 265 (*M* − PhS, 96%), 180 (*M* − PhS − [CH_2]$_5$Me, 20), 110 (PhSH, 64) (Found: C, 70.5; H, 8.15; S, 16.8. $C_{22}H_{30}OS_2$ requires C, 70.5; H, 8.07; S, 17.1%).

1-*Phenyl*-2,2-*bis*(*phenylthio*)*butan*-1-*ol* (14; R^1 = Et, R^2 = Ph). 1,1-Bis(phenylthio)propane (0.86 g, 3.3 mmol), TMEDA (0.48 g, 0.58 ml, 0.41 mmol), n-butyl-lithium (1.44M in hexane; 2.7 ml, 0.39 mmol), and benzaldehyde (method C) gave the *alcohol* (1.07 g, 89%) as an oil, R_F (CH_2Cl_2) 0.58, $\nu_{max.}$ (liq) 3 460br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.2 (15 H, m, 2 × PhS and Ph), 4.70 (1 H, d, *J* 2.5 Hz, C*H*OH, collapses to s with D_2O), 3.30 (1 H, d, *J* 2.5 Hz, CHO*H*, removed by D_2O), 1.51 (2 H, m, CH_2Me), and 1.06 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 259 (*M* − PhCHOH, 35%), 256 (*M* − PhS, 94), and 110 (PhSH, 100) (Found: *M* − PhCHOH, 159.061 0. $C_{15}H_{15}S_2$ requires 259.061 4. Found: *M* − PhSH, 256.092 0. $C_{16}H_{16}O$ requires 256.092 1).

Phenyl-2,2-*bis*(*phenylthio*)-[1-^{2}H]*butan*-1-*ol* (19; R^1 = Et, R^2 = Ph, R^3 = ^{2}H). 1,1-Bis(phenylthio)propane (781 mg, 3 mmol), TMEDA (0.5 ml, 3.6 mmol), n-butyl-lithium (1.6M in hexane; 2 ml, 3.2 mmol) and [*formyl*-^{2}H]benzaldehyde [44] (method C) gave the *alcohol* (570 mg, 52%) as an oil, R_F (CH_2Cl_2) 0.62, $\nu_{max.}$ (liq) 3 450br (OH) and 1 579 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.0 (15 H, m, 2 × SPh and Ph). 3.35 (1 H, s, OH, removed by D_2O), 1.7—1.0 (2 H, m, C*H*$_2$Me), 1.02 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 259 (*M* − PhCDOH, 72), 258 (*M* − PhS, 67), 109 (PhS, 72) (Found: *M* − PhCDOH, 259.062 0. $C_{15}H_{15}S_2$ requires 259.061 5. Found: *M* − PhS, 258.106 5. $C_{16}H_{16}DOS$ requires 258.106 5).

2-*Methyl*-1-*phenyl*-3,3-*bis*(*phenylthio*)*pentan*-2-*ol* (19; R^1 = Et, R^2 = Me, R^3 = $PhCH_2$). 1,1-Bis(phenylthio)-propane (1.3 g, 5 mmol), TMEDA (0.78 ml, 5.4 mmol), n-butyl-lithium (2.8M in hexane; 2.0 ml, 5.6 mmol) and benzyl methyl ketone (method C) gave an oil. Crystallisation from light petroleum (b.p. 60—80 °C) gave the *alcohol* (1.1 g, 56%), m.p. 84—85 °C, R_F (CH_2Cl_2) 0.62, $\nu_{max.}$ (liq) 3 520br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.64—7.16 (15 H, m, 2 × SPh and Ph), 3.29 and 3.10 (2 H, ABq, *J* 14 Hz, PhCH_AH_B), 2.41 (1 H, s, OH, removed by D_2O), 1.78 (2 H, q, *J* 7 Hz, C*H*$_2$Me), 1.30 (3 H, s, *Me*COH), and 1.20 (3 H, t, *J* 7 Hz, CH_2*Me*) (Found: C, 73.3; H, 6.95; S, 16.0. $C_{24}H_{26}OS_2$ requires C, 73.1; H, 6.64; S, 16.25%).

1-[1,1-*Bis*(*phenylthio*)*propyl*]*cyclohexanol* (19; R^1 = Et, R^2R^3 = [CH_2]$_5$). 1,1-Bis(phenylthio)propane (0.65 g, 2.5 mmol), TMEDA (0.39 ml, 2.7 mmol), n-butyl-lithium (2.44M in hexane; 1.2 ml, 2.9 mmol) and cyclohexanone (method C) gave an oil. Crystallisation from light petroleum (b.p. 60—80 °C) gave the *alcohol* (0.61 g, 68%), m.p. 60—61 °C, R_F (CH_2Cl_2) 0.56, $\nu_{max.}$ ($CHCl_3$) 3 520br (OH) and 1 581 cm^{-1} (PhS), δ($CDCl_3$) 7.6—7.1 (10 H, m, 2 × SPh), 2.26 (1 H, s, OH, removed by D_2O), 2.0—1.4 (12 H, m, C*H*$_2$Me and cyclohexyl), and 1.10 (3 H, t, *J* 4 Hz, CH_2*Me*), *m/e* 259 [$(PhS)_2CEt$, 6%], 249 (*M* − SPh, 38) and 110 (PhSH, 100) (Found: C, 70.2; H, 7.25, S. 18.1. $C_{21}H_{26}OS_2$ requires C, 70.3; H, 7.31; S, 17.9%).

2-*Phenyl*-3,3-*bis*(*phenylthio*)*hexan*-2-*ol* (19; R^1 = Pr^n, R^2 = Ph, R^3 = Me). 1,1-Bis(phenylthio)butane (0.69 g, 2.5 mmol), TMEDA (0.39 ml, 2.7 mmol), n-butyl-lithium (1.8M in hexane; 1.5 ml, 2.7 mmol), and acetophenone (method C) gave the *alcohol* (410 mg, 42%, 80% based on recovered starting material) as an oil, R_F (CH_2Cl_2) 0.57, $\nu_{max.}$ (liq) 3 470br (OH) and 1 579 cm^{-1} (PhS), δ($CDCl_3$) 8.0—7.1 (15 H, m, 2 × SPh and Ph), 3.18 (1 H, s, OH), 2.03 (3 H, s, PhC*Me*), 2.0—1.3 (4 H, m, 2 × CH_2), and 0.60 (3 H, t, *J* 6 Hz, CH_2*Me*), *m/e* 285 (*M* − SPh, 19%), 273 [*M* − MeC(Ph)OH, 89], 175 (*M* − SPh − PhSH, 100), 121 [MeC(Ph)OH, 33], 110 (PhSH, 74), and 77 (Ph, 67) (Found: C, 73.3; H, 6.9; S, 16.0. $C_{24}H_{26}OS_2$ requires C, 73.1; H, 6.64; S, 16.2%).

3-*Methyl*-1-*phenyl*-2,2-*bis*(*phenylthio*)*butan*-1-*ol* (14; R^1 = Pr^i, R^2 = Ph). 1,1-Bis(phenylthio)-2-methyl-propane (1.38 g, 5 mmol), TMEDA (0.83 ml, 6 mmol), n-butyl-lithium (1.6M in hexane; 3.3 ml, 5.26 mmol), and benzaldehyde (method C) gave an oil (1.36 g, 72%). Crystallisation from light petroleum (b.p. 60—80 °C) gave the *alcohol*, m.p. 98—99 °C, R_F (CH_2Cl_2) 0.62, $\nu_{max.}$ (liq) 3 460br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.72—7.06 (15 H, m, 2 × SPh and Ph), 4.98 (1 H, d, *J* 2.5 Hz, C*H*OH, collapses to s with D_2O), 3.51 (1 H, d, *J* 2.5 Hz, CHO*H*, removed by D_2O), 2.15 (1 H, sept, *J* 3.5 Hz, C*H*Me_2), and 1.09 (6 H, d, *J* 3.5 Hz, CH*Me*$_2$), *m/e* 273 (*M* − SPh, 2%), 271 (*M* − PhCHOH, 4), 110 (PhSH, 11), and 43 ($CHMe_2$, 100) (Found: C, 72.3; H, 6.25; S, 16.5; $C_{23}H_{24}OS_2$ requires C, 72.6; H, 6.35; S, 16.8%).

3,3-*Bis*(*phenylthio*)*heptan*-2-*ol* (14; R^1 = Bu^n, R^2 = Me). 1,1-Bis(phenylthio)pentane (1.33 g, 5 mmol), TMEDA (0.78 ml, 5.4 mmol), n-butyl-lithium (2.8 M in hexane; 2 ml, 5.6 mmol), lithium bromide (1 g), and acetaldehyde (method B) gave the *alcohol* (0.94 g, 62%) as an oil, R_F (CH_2Cl_2) 0.47, $\nu_{max.}$ (liq) 3 480br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.9—7.0 (10 H, m, SPh), 3.87 (1 H, q, *J* 6 Hz, C*H*Me), 2.58 (1 H, s, OH, removed by D_2O), 1.9—0.9 (6 H, m, 3 × CH_2), 1.36 (3 H, d, *J* 6 Hz, CH*Me*), and 0.86 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 287 (*M* − Me, 6%), 223 (*M* − PhS, 76), 110 (PhSH, 100) (Found: C, 68.3; H, 7.35; S, 19.1. $C_{19}H_{24}OS_2$ requires C, 68.6; H, 7.28; S, 19.3%).

2,6-*Dimethyl*-3,3-*bis*(*phenylthio*)*heptan*-2-*ol* (19; R^1 = 3-Me-butyl, R^2 = R^3 = Me). 4-Methyl-1,1-bis(phenyl-thio)pentane (0.30 g, 1 mmol), TMEDA (0.2 ml, 1.3 mmol), n-butyl-lithium (2.4 M in hexane; 0.5 ml 1.2 mmol) and acetone (method C) gave an oil (256 mg, 71%). Crystal-lisation from aqueous ethanol gave the *alcohol*, m.p. 64—65 °C, R_F (CH_2Cl_2) 0.31, $\nu_{max.}$ (liq) 3 480br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.1 (10 H, m, 2 × SPh), 2.62 (1 H, s, OH, removed by D_2O), 1.8—1.3 (5 H, m, CH_2CH_2-CH) overlain by 1.46 (6 H, s, *Me*$_2$COH), and 0.76 (6 H, d, *J* 6 Hz, CH*Me*$_2$), *m/e* 360 (M^+, 4%), 301 (*M* − Me_2COH, 18), 251 (*M* − SPh, 100), 110 (PhSH, 60) (Found: C, 69.8; H, 7.65; S, 17.5. $C_{21}H_{28}OS_2$ required C, 70.0; H, 7.83; S, 17.8%).

1-*Phenyl*-2,2-*bis*(*phenylthio*)*pentan*-3-*ol* (14; R^1 = Ph-

CH_2, R^2 = Et). 2-Phenyl-1,1-bis(phenylthio)ethane (1.61 g, 5 mmol), TMEDA (0.78 ml, 5.4 mmol), n-butyl-lithium (1.6M in hexane; 3.5 ml, 5.6 mmol), and propionaldehyde (method C) gave the *alcohol* (1.21 g, 64%) as an oil, R_F (CH_2Cl_2) 0.60, $\nu_{max.}$ (liq) 3 480br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.8—7.0 (15 H, m, 2 × SPh and Ph), 3.54 (1 H, dd, *J* 2 and 10 Hz, CH^*_2CHOH), 3.16 (2 H, ABq, *J* 14 Hz, CH_AH_BPh), 2.35 (1 H, s, OH, removed by D_2O), 2.2—1.3 (2 H, m, $MeCH_2CHOH$), and 0.90 (3 H, t, *J* 7 Hz, CH_2Me), *m/e* 321 (*M* − EtCHOH, 3%), 271 (*M* − SPh, 48), 161 (*M* − PhSH − PhS, 65), 110 (PhSH, 100), and 91 ($PhCH_2$, 92) (Found: *M* − EtCHOH, 321.0787. $C_{20}H_{17}S_2$ requires 321.077 2. Found: *M* − SPh, 271.114 1. $C_{17}H_{19}OS$ requires 271.115 7).

1,2-*Diphenyl*-2,2-*bis*(*phenylthio*)*ethanone* (22). n-Butyl-lithium (1.6M in hexane; 1.5 ml, 2.4 mmol) was added to a stirred solution of 1-phenylbis(phenylthio)methane (616 mg, 2 mmol) in dry THF (20 ml) under nitrogen at −78 °C to give a yellow solution. After 10 min benzoyl chloride (0.25 ml, 2.2 mmol) was added and the solution allowed to warm to room temperature over 1.5 h. The mixture was then poured into water (30 ml) and extracted with ether (3 × 20 ml), the extract washed with water (2 × 10 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give a yellow oil. Crystallisation from ethanol (*ca.* 50 ml) gave the bis-(α-phenylthio)ketone (22) (814 mg, 66%) as needles, m.p. 138—139 °C (lit.,[18] m.p. 138—139 °C).

1,2-*Diphenyl*-1,1-*bis*(*phenylthio*)*ethanol* (14; $R^1 = R^2$ = Ph). Zinc borohydride[45] (1N-solution in ether; 10 ml, 10 mmol) was added to a stirred solution of 1,2-diphenyl-2,2-bis(phenylthio)ethanone (22) (412 mg, 1 mmol) in dry ether (10 ml) under nitrogen. After 46 h the reaction mixture was poured into saturated ammonium chloride (25 ml), extracted with ether (3 × 20 ml), the extract washed with water (2 × 10 ml), dried, and evaporated *in vacuo* to give an oil, which was purified by preparative t.l.c. to give the *alcohol* (246 mg, 60%) as an oil, R_F (CH_2Cl_2) 0.60, $\nu_{max.}$ (liq) 3 460br (OH) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.7—6.6 (20 H, m, 2 × SPh and 2 × Ph), 4.83 (1 H, d, *J* 2 Hz, CHOH collapses to s with D_2O), and 3.80 (1 H, d, *J* 2 Hz, CHO*H*, removed by D_2O), *m/e* 307 (*M* − PhCHOH, 45%), 305 (*M* − PhS, 30), 110 (PhSH, 100), and 77 (Ph, 90) (Found: C, 75.2; H, 5.6; S, 15.2. $C_{26}H_{22}OS_2$ requires C, 75.3; H, 5.35; S, 15.5%).

Synthesis of Ketones from Aldehyde Adducts (14).—*Pentan*-2-*one*. The alcohol (14; R^1 = Me, R^2 = Et) (100 mg) was dissolved in TFA (0.4 ml) in an n.m.r. tube. The n.m.r. spectrum of the mixture was run immediately and showed mainly pentan-2-one (*ca.* 90%), identical with an authentic sample, plus diphenyl disulphide, δ(TFA) 2.61 (2 H, t, *J* 7 Hz, $COCH_2CH_2$), 2.32 (3 H, s, CO*Me*), 1.69 (2 H, sext, *J* 7 Hz, CH_2CH_2Me), and 0.96 (3 H, t, *J* 7 Hz, CH_2Me). N.B. The other product was the α-(phenylthio)ketone (16; R^1 = Me, R^2 = Et) or (30; $R^2 = R^4$ = Me) (*ca.* 10%), which was unchanged in the reaction mixture after 15 min.

1-*Phenylpropan*-2-*one*. The alcohol (14; R^1 = Me, R^2 = Ph) (273 mg) was dissolved in TFA (4 ml); diphenyl disulphide precipitated almost immediately. The mixture was stirred with cooling in ice–water for 5 min and then evaporated *in vacuo* to give an oil. Preparative t.l.c. (CH_2Cl_2) gave 1-phenylpropan-2-one (90 mg, 87%) identical with an authentic sample, $\nu_{max.}$ (liq) 1 712 cm^{-1} (C=O), δ($CDCl_3$) 7.29 (5 H, s, Ph), 3.68 (2 H, s, CH_2Ph), and 2.12 (3 H, s, Me).

Pentan-3-*one*. The alcohol (14; R^1 = Et, R^2 = Me) (90 mg) was dissolved in TFA (1 ml) and after stirring at 0 °C for a few minutes the mixture was filtered to remove the precipitate of diphenyl disulphide. The filtrate had an n.m.r. spectrum which was essentially the same as that of the authentic sample of pentan-3-one (*ca.* 90%), δ(TFA) 2.70 (4 H, q, *J* 8 Hz, 2 × CH_2Me) and 1.20 (6 H, t, *J* 8 Hz, 2 × CH_2Me). N.B. The other product was the α-(phenylthio)ketone (16; R^1 = Et, R^2 = Me) or (30, R^2 = Et, R^4 = H) (*ca.* 10%), which was unchanged in the reaction mixture after 15 min.

Decan-3-*one*. Prepared in a similar way to 1-phenylpropan-2-one but using the alcohol (14; R^1 = Et, R^2 = n-hexyl) (228 mg), decan-3-one[46] (29 mg, 31%) was an oil, $\nu_{max.}$ (liq) 1 714 cm^{-1} (C=O), δ($CDCl_3$) 2.65—2.20 (4 H, m, CH_2COCH_2) and 1.75—0.86 (16 H, m, $Me[CH_2]_5$ and $COCH_2Me$), *m/e* 156 (M^+, 9%), 127 (*M* − Et, 45), and 57 (EtCO, 100).

1-*Phenylbutan*-2-*one*.—Prepared in a similar way to 1-phenylpropan-2-one but using the alcohol (14; R^1 = Et, R^2 = Ph) (251 mg), the ketone[47] (75 mg, 74%) was an oil, $\nu_{max.}$ (liq) 1 713 cm^{-1} (C=O), δ($CDCl_3$) 7.27 (5 H, s, Ph), 3.67 (2 H, s, CH_2Ph), 2.46 (2 H, q, *J* 7 Hz, CH_2Me), and 1.02 (3 H, t, *J* 7 Hz, CH_2Me).

3-*Methyl*-1-*phenylbutan*-2-*one*. Prepared in a similar way to 1-phenylpropan-2-one but using the alcohol (14; $R^1 = Pr^i$, R^2 = Ph) (317 mg) the ketone[48] (68 mg, 92%) was an oil, $\nu_{max.}$ (liq) 1 710 cm^{-1} (C=O), δ($CDCl_3$) 7.4—7.06 (5 H, m, Ph), 3.71 (2 H, s, CH_2Ph), 2.69 (1 H, sept, *J* 6.5 Hz, $CHMe_2$), and 1.07 (6 H, d, *J* 6 Hz, $CHMe_2$).

Heptan-3-*one*. The alcohol (14; $R^1 = Bu^n$, R^2 = Me) (76 mg) was dissolved in TFA (0.35 ml) in an n.m.r. tube. The n.m.r. spectrum was run immediately and showed mainly heptan-3-one[46] (*ca.* 80%), plus diphenyl disulphide δ(TFA) 2.9—2.4 (4 H, m, CH_2COCH_2) and 2.0—0.75 (10 H, m, CH_2CH_2Me and $COCH_2Me$). N.B. The other product was the α-(phenylthio)ketone (16; $R^1 = Bu^n$, R^2 = Me) or (30; $R^2 = Bu^n$, R^4 = H) (*ca.* 20%).

Experiments on the Mechanisms of the TFA Reaction.—2,3-*Bis*(*phenylthio*)*pent*-3-*ene* (33; $R^2 = R^4$ = Me). Thionyl chloride (0.12 ml, 1.65 mmol) was added to an ice-cooled solution of the alcohol (14; R^1 = Et, R^2 = Me) (293 mg, 0.97 mmol) in carbon tetrachloride (12 ml) and triethylamine (0.8 ml, 5.7 mmol) in a foil-wrapped flask. After 1 min the mixture was poured into dilute hydrochloric acid (20 ml) and extracted with carbon tetrachloride (3 × 10 ml). The extract was washed with water (2 × 10 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give an oil which was purified by preparative t.l.c. to give the *bis-sulphide* (250 mg, 90%), as an oil, R_F (CH_2Cl_2) 0.77, $\nu_{max.}$ (liq) 1 628 (C=C) and 1 585 cm^{-1} (PhS), n.m.r. showed a 1 : 1 mixture of geometric isomers A and B, δ($CDCl_3$) 7.6—6.9 (10 H, m, 2 × SPh), 6.12^A and 5.66^B (1 H, each q, *J* 7 Hz, C=C*H*Me), 4.41^B and 3.85^A (1 H, each q, *J* 7 Hz, PhSC*H*Me), 1.74^A and 1.47^B (3 H, each d, *J* 7 Hz, C=CHMe), and 1.45 (3 H, d, PhSCH*Me*), *m/e* 286 (M^+, 48%), 177 (*M* − SPh, 60), 149 (*M* − PhSCHMe, 100), and 110 (PhSH, 38) (Found: C, 71.0; H, 6.7; S, 22.7. $C_{17}H_{18}S_2$ requires C, 71.3; H, 6.33; S, 22.4%). After standing in sunlight for 1 or 2 days only isomer A remained.

Reaction of 2,3-*bis*(*phenylthio*)*pent*-3-*ene with TFA*. The bis-sulphide (33; $R^2 = R^4$ = Me) (60 mg) was dissolved in TFA (0.35 ml) in an n.m.r. tube. The n.m.r. spectrum of the mixture was run immediately and showed only pentan-3-one (100%), identical with an authentic sample, plus

diphenyl disulphide, δ(TFA) 2.70 (4 H, q, *J* 8 Hz, 2 CH_2Me) and 1.20 (6 H, t, *J* 8 Hz, 2 × CH_2Me).

Reaction of 2-phenylthiopentan-3-one with TFA. The α-(phenylthio)ketone (30; $R^2 = R^4 =$ Me) (56 mg, 0.29 mmol) was dissolved in TFA (0.3 ml) in an n.m.r. tube. After 15 min benzenethiol (33 mg, 0.3 mmol) was added and the mixture shaken. After a further 20 min, conversion to pentan-3-one was essentially complete (n.m.r.).

Reaction of 2,3-bis(phenylthio)pent-3-ene with aqueous TFA. The bis-sulphide (33; $R^2 = R^4$ = Me) (60 mg) was dissolved in aqueous TFA (10% solution of water in TFA; 0.35 ml) in an n.m.r. tube. The n.m.r. spectrum was run immediately and showed a mixture of pentan-3-one (*ca.* 80%) and 2-phenylthiopentan-3-one (30; $R^2 = R^4$ = Me) (*ca.* 20%).

Reaction of 3,3-bis(phenylthio)pentan-2-ol with TFA–TFA anhydride. The alcohol (14; R^1 = Et, R^2 = Me) (70 mg) was dissolved in TFA–TFA anhydride (0.35 ml; 1 : 1) in an n.m.r. tube. The n.m.r. spectrum was run immediately and showed a mixture of 2,3-bis(phenylthio)pent-3-ene (33; $R^2 = R^4$ = Me) (*ca.* 40%), pentan-3-one (*ca.* 20%) and 3-phenylthiopentan-2-ole (16; R^1 = Et, R^2 = Me) (*ca.* 40%).

Reaction of ketone adducts (19) *with TFA.* (a) *1-Cyclohexylpropanone* (24). Prepared in a similar way to 1-phenylpropan-2-one but using the alcohol (19; R^1 = Et, $R^2R^3 = [CH_2]_5$) (299 mg) to give the ketone [49] (75 mg, 64%) as an oil, $\nu_{max.}$ (liq) 1 709 cm^{-1} (C=O), δ($CDCl_3$) 2.49 (2 H, q, *J* 7 Hz, CH_2Me), 2.1—1.08 (11 H, m, cyclohexyl), and 1.05 (3 H, t, *J* 7 Hz, CH_2Me).

(b) *(Phenylthiomethylene)cyclopentane.* Trifluoroacetic acid (2 ml) was added to the alcohol (19; R^1 = H, $R^2R^3 = [CH_2]_4$) (185 mg, 0.58 mmol) and the mixture stirred for 15 s, poured into saturated sodium carbonate (20 ml) and extracted with ether (3 × 10 ml). The extract was washed with water (2 × 5 ml), dried ($MgSO_4$), and evaporated *in vacuo* to give an oil. Preparative t.l.c. (CH_2Cl_2) gave a compound tentatively identified as the vinyl sulphide (38 mg, 42% based on recovered starting material) as an oil, R_F (CH_2Cl_2) 0.82, δ($CDCl_3$) 7.4—6.9 (5 H, m, Ph), 6.02 (1 H, m, C=CH), and 3.0—2.0 (8 H, m, cyclopentyl), *m/e* 190 (M^+, 9%) and 110 (PhSH, 100).

(c) *2-Ethyl-2-phenylthiopentan-3-one.* (20; R^1 = Me, $R^2 = R^3$ = Et). The alcohol (19; R^1 = Me, $R^2 = R^3$ = Et) (120 mg) was dissolved in TFA (3 ml), and diphenyl disulphide precipitated almost immediately. The mixture was stirred with cooling in an ice-bath for 6 min, poured into saturated sodium carbonate (30 ml) and extracted with ether (3 × 10 ml). The extract was washed with water (2 × 5 ml), dried, and evaporated to give an oil which was purified by preparative t.l.c. to give the α-(*phenylthio*)-*ketone* (40 mg, 50%) as an oil, R_F (CH_2Cl_2) 0.66, $\nu_{max.}$ (liq) 1 698 cm^{-1} (C=O), δ($CDCl_3$) 7.28 (5 H, s, SPh), 3.1—2.4 (2 H, m, MeCH_2CO), 2.02—1.48 (2 H, m, PhSCCH_2Me), 1.32 (3 H, s, PhSCMe), 1.09 (3 H, t, *J* 7 Hz, COCH_2Me), and 0.90 (3 H, t, *J* 8 Hz, PhSCCH_2Me), *m/e* 222 (M^+, 8%), 165 (M − EtCO, 100), 123 (M − SPh, 12), 109 (PhS, 11), and 57 (EtCO, 7) (Found: C, 69.8; H, 7.85; S, 14.5. $C_{13}H_{18}OS$ requires C, 70.2; H, 8.16; S, 14.4%).

1-Phenylthio-1-p-tolylpropan-2-one (20; R^1 = H, R^2 = Me, R^3 = *p*-MeC_6H_4). The alcohol (19; R^1 = H, R^2 = Me, R^3 = p-MeC_6H_4) (222 mg) was dissolved in TFA (5 ml). Reaction and work-up as above gave the α-(*phenylthio*)*ketone* (80 mg, 52%) as an oil, R_F (CH_2Cl_2) 0.57, $\nu_{max.}$ (liq) 1 711 (C=O) and 1 578 cm^{-1} (PhS), δ($CDCl_3$) 7.4—6.9 (9 H, m, SPh and C_6H_4), 4.82 (1 H, s, PhSCH), 2.32 (3 H, s, C_6H_4Me), and 2.08 (3 H, s, MeCO), *m/e* 256 (M^+, 3%), 213 (M − MeCO, 100), 165 (M − SPh, 4), 110 (PhSH, 7), and 91 (C_6H_4Me, 7) (Found: M^+, 256.091 3. $C_{16}H_{16}OS$ requires M, 256.092 2).

3-Phenylmethyl-3-phenylthiopentan-2-one (20; R^1 = Et, R^2 = Me, $R^3 = CH_2$Ph). Similarly, the alcohol (19; R^1 = Et, R^2 = Me, $R^3 = CH_2$Ph) (468 mg) and TFA (3 ml) gave the α-(*phenylthio*)*ketone* (310 mg, 91%) as an oil, R_F (CH_2Cl_2) 0.8, $\nu_{max.}$ (liq) 1 692 (C=O) and 1 581 cm^{-1} (PhS), δ($CDCl_3$) 7.6—7.25 (10 H, m, Ph and SPh), 3.32 and 2.96 (2 H, ABq, *J* 15 Hz, CH_2Ph), 243 (3 H, s, MeCO), 1.61 (2 H, q, *J* 7 Hz, CH_2Me), and 1.00 (3 H, t, *J* 7 Hz, CH_2Me) *m/e* 284 (M^+, 7%), 241 (M − MeCO, 100), and 110 (PhSH, 80) (Found: M^+, 284.123 4. $C_{18}H_{20}OS$ requires 284.123 5).

3-Phenyl-3-phenylthiohexan-2-one (20; $R^1 = Pr^n$, R^2 = Me, R^3 = Ph). Similarly, the alcohol (19; $R^1 = Pr^n$ R^2 = Me, R^3 = Ph) (65 mg) and TFA (2 ml) gave the α-(*phenylthio*)*ketone* (41 mg, 87%) as an oil, R_F (CH_2Cl_2) 0.8, $\nu_{max.}$ (liq) 1 700 (C=O) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.5—7.1 (10 H, m, PhS and Ph), 2.16 (3 H, s, MeCO), 1.78 (2 H, q, *J* 7 Hz, CH_2CH$_2$Me), 1.6—1.0 (2 H, m, CH_2CH_2Me), and 0.81 (3 H, t, *J* 7 Hz, CH_2Me), *m/e* 284 (M^+, <1%), 241 (M − Pr^n and M − MeCO, 100), and 110 (PhSH, 49) (Found: M^+, 284.124 2. $C_{18}H_{22}OS$ requires M, 284.123 5).

α-(Phenylthio)ketones by Treatment of (14) *with* TsOH.—*1-Phenylthiobutan-2-one* * (16; R^1 = H, R^2 = Et). Toluene-*p*-sulphonic acid (132 mg, 0.7 mmol) was added to the alcohol (14; R^1 = H, R^2 = Et) (122 mg, 0.42 mmol) heated under reflux in benzene (10 ml). After 15 min, the solution was cooled, poured into saturated sodium carbonate (20 ml), extracted with ether (3 × 10 ml), the extract washed with water (2 × 10 ml), dried ($MgSO_4$), and evaporated to give an oil, which was purified by preparative t.l.c. to give the ketone (54 mg, 71%) as an oil, R_F (CH_2Cl_2) 0.45, δ($CDCl_3$) 7.5—7.1 (5 H, s, SPh), 3.68 (2 H, s, CH_2SPh), 2.62 (2 H, q, *J* 7.5 Hz, CH_2Me), and 1.06 (3 H, t, *J* 7.5 Hz, CH_2Me).

3-Methyl-2-phenylthiobutan-2-one † (16; R^1 = H, $R^2 = Pr^i$). Similarly the alcohol (14; R^1 = H, $R^2 = Pr^i$) (135 mg) gave the ketone (57 mg, 66%) as an oil, R_F (CH_2Cl_2) 0.6, $\nu_{max.}$ (liq) 1 705 (C=O) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.6—7.1 (5 H, m, SPh), 3.75 (2 H, s, PhSCH_2 2.89 (1 H, sept, *J* 7 Hz, CHMe$_2$), and 1.10 (6 H, d, *J* 7 Hz, CHMe_2).

1-Phenylthio-octan-2-one. (16; R^1 = H, R^2 = n-hexyl). Similarly the alcohol (14; R^1 = H, R^2 = n-hexyl) (151 mg) gave the *ketone* (63 mg, 61%) as an oil, R_F (CH_2Cl_2) 0.57, $\nu_{max.}$ (liq) 1 708 (C=O) and 1 585 cm^{-1} (PhS), δ($CDCl_3$) 7.4—7.1 (5 H, m, SPh), 3.65 (2 H, s, CH_2SPh), 2.58 (2 H, t, *J* 7 Hz, CH_2CH_2CO), 1.8—1.1 (8 H, m, $[CH_2]_4$ Me), and 0.87 (3 H, distorted t, *J* 6 Hz, Me), *m/e* 236 (M^+, 50%), 123 (PhSCH_2, 70), 113 (M − PhSCH_2, 100), 110 (PhSH, 48), 85 (Me$[CH_2]_4$), and 32 (Found: M^+, 236.123 4. $C_{14}H_{20}OS$ requires M, 236.123 4).

3-Phenylthiobutan-2-one ‡ (16; $R^1 = R^2$ = Me). Likewise the alcohol (14; $R^1 = R^2$ = Me) (90 mg) gave the ketone (46 mg, 82%) as an oil, R_F (CH_2Cl_2) 0.44, δ($CDCl_3$) 7.20 (5 H, s, Ph), 3.60 (1 H, q, *J* 7 Hz, CHMe), 2.18 (3 H, s, MeCO), and 1.36 (3 H, d, *J* 7 Hz, CHMe).

* The preparation of this compound by a different method has been announced in a preliminary communication.[21]

† This compound has been prepared from the corresponding α-chloro-ketone, see ref. 50.

‡ This compound has been prepared from the corresponding α halo-ketone, see ref. 51.

2-*Phenylthiopentan*-3-*one* (16; R^1 = Me, R^2 = Et). Likewise the alcohol (14; R^1 = Me, R^2 = Et) (216 mg) gave the *ketone* (115 mg, 84%) as an oil, R_F (CH_2Cl_2) 0.59, $\nu_{max.}$ (liq) 1 703 (C=O) and 1 579 cm^{-1} (PhS), δ($CDCl_3$) 7.5—7.1 (5 H, m, PhS), 3.78 (1 H, q, *J* 7.5 Hz, C*H*Me), 3.0—2.2 (2 H, m, MeCH_2CO), 1.40 (3 H, d, *J* 7.5 Hz, CH*Me*), and 1.05 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 194 (M^+, 50%), 139 (*M* − EtCO, 100), and 109 (PhS, 18) (Found: M^+, 194.076 9. $C_{11}H_{14}OS$ requires *M*, 194.076 5).

2-*Phenylthiohexan*-3-*one*. (16; R^1 = Me, R^2 = Me, R^2 = Pr^n). Similarly, the alcohol (14; R^1 = Me, R^2 = Pr^n) (150 mg) gave the *ketone* (79 mg, 81%) as an oil, R_F (CH_2Cl_2) 0.60, $\nu_{max.}$ (liq) 1 705 (C=O) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.5—7.1 (5 H, m, SPh), 3.78 (1 H, q, *J* 7 Hz, C*H*Me), 2.60 (2 H, dt, *J* 3 and 7 Hz, CH_2CH_2CO), 1.60 (2 H, sext, *J* 7 Hz, CH_2CH_2Me), 1.41 (3 H, d, *J* 7 Hz, CH*Me*), and 0.90 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 208 (M^+, 18%), 137 (*M* − Pr^nCO, 100), and 109 (PhS, 19) (Found: C, 69.2; H, 7.75; S, 15.1. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.74; S, 15.4%).

1-*Phenyl*-2-(*phenylthio*)*propanone* * (16; R^1 = Me, R^2 = Ph). In the same way, the alcohol (14; R^1 = Me, R^2 = Ph) (192 mg) gave the *ketone* (84 mg, 64%) as an oil, R_F (CH_2Cl_2) 0.62 $\nu_{max.}$ (liq) 1 679 (C=O) and 1 581 cm^{-1} (PhS), δ($CDCl_3$) 8.2—7.1 (10 H, m, SPh, and Ph), 4.63 (1 H, q, *J* 7 Hz, C*H*Me), and 1.51 (3 H, d, *J* 7 Hz, CH*Me*).

3-*Phenylthiopentan*-2-*one* (16, R^1 = Et, R^2 = Me). Likewise, the alcohol (14; R^1 = Me, R^2 = Et) (115 mg) gave the *ketone* (59 mg, 80%) as an oil, R_F (CH_2Cl_2) 0.50, $\nu_{max.}$ (liq) 1 708 (C=O) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.32 (5 H, m, PhS), 3.55 (1 H, t, *J* 7 Hz, C*H*CH_2), 2.24 (3 H, s, *Me*CO), 2.0—1.55 (2 H, m, CHCH_2Me), and 1.04 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 194 (M^+, 40%), 151 (*M* − MeCO, 90), 109 (PhS, 100), and 43 (MeCO, 75) (Found: M^+, 194.076 6. $C_{11}H_{14}OS$ requires *M*, 194.076 5).

4-*Phenylthiohexan*-3-*one* (16; R^1 = R^2 = Et). Similarly the alcohol (14; R^1 = R^2 = Et) (185 mg) gave the *ketone* (87 mg, 72%) as an oil, R_F (CH_2Cl_2) 0.59, $\nu_{max.}$ (liq) 1 704 (C=O) and 1 581 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.0 (5 H, m, SPh), 3.56 (1 H, t, *J* 8 Hz, C*H*CH_2), 2.8—2.4 (2 H, m, MeCH_2CO), 2.1—1.5 (2 H, m, CHCH_2Me), and 1.03 and 1.00 (6 H, each t, *J* 7 and 7.5 Hz, 2 × Me), *m/e* 208 (M^+, 34%), 151 (*M* − EtCO, 100) and 110 (PhSH, 34) (Found: C, 69.7; H, 7.8; S, 15.6. $C_{12}H_{16}OS_2$ requires C, 69.2; H, 7.76; S, 15.4%).

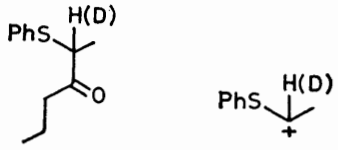
3-*Phenylthiodecan*-4-*one* (16; R^1 = Et, R^2 = n-hexyl). In the same way the alcohol (14; R^1 = Et, R^2 = n-hexyl) (133 mg) gave the *ketone* (54 mg, 58%) as an oil, R_F (CH_2Cl_2) 0.67, $\nu_{max.}$ (liq) 1 707 (C=O) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.5—7.1 (5 H, m, SPh), 3.55 (1 H, t, *J* 7 Hz, PhSC*H*CH_2), 2.56 (2 H, t, *J* 7 Hz, COCH_2CH_2), 2.1—1.12 (10 H, m, CHCH_2Me and [CH_2]$_4$Me), 1.00 (3 H, t, *J* 7 Hz, $CHCH_2$*Me*), and 0.86 (3 H, t, *J* 7 Hz, Me), *m/e* 264 (M^+, 25%), 151 (PhSCHEt, 100), 109 (PhS, 23), and 85 (Me-[CH_2]$_5$, 48) (Found: C, 73.1; H, 9.3; S, 11.7. $C_{16}H_{24}OS$ requires C, 72.9; H, 9.15; S, 12.1).

3-*Phenylthioheptan*-2-*one* (16; R^1 = Bu^n, R^2 = Me). Similarly, the alcohol (14; R^1 = Bu^n, R^2 = Me) (173 mg) gave the *ketone* (91 mg, 78%) as an oil, R_F (CH_2Cl_2) 0.62, $\nu_{max.}$ (liq) 1 705 (C=O) and 1 581 cm^{-1} (PhS), δ($CDCl_3$) 7.6—7.0 (5 H, m, SPh), 3.49 (1 H, t, *J* 7 Hz, C*H*CH_2), 2.14 (3 H, s, *Me*CO), 2.0—1.1 (6 H, m, 3 × CH_2), and 1.04—0.74 (3 H, m, CH_2*Me*), *m/e* 222 (M^+, 43%), 179 (*M* − MeCO, 100), and 110 (PhSH, 43) (Found: M^+, 222.108 0. $C_{13}H_{18}OS$ requires *M*, 222.107 7).

Experiments on the Mechanism of the Reaction of (14) *with* TsOH.—*Reaction of* [3-^{2}H]-2,2-*bis*(*phenylthio*)*hexan*-3-*ol with* TsOH. (*a*) Toluene-*p*-sulphonic acid (45 mg, 0.24 mmol) was added to the alcohol (48, 72 mg, 0.23 mmol) heated under reflux in benzene (5 ml). After 6 min, work-up as before gave 2-phenylthiohexan-3-one (16; R^1 = Me, R^2 = Pr^n) (40 mg, 85%) which mass spectrometry showed to be 37% deuteriated in the 2-position. (*b*) The experiment was repeated and samples taken from the reaction mixture after 0.5, 1, 2, 4, and 6 min and the mass spectra run without work-up. Mass spectra were also obtained after work-up, both before and after preparative t.l.c. The results obtained are summarised in Table 6,

TABLE 6

Mass spectra of deuteriated 2-phenylthiohexan-3-one



Time/min	Deuteriation (%)	Deuteriation (%)
0.5	41	34
1	43	34
2	40	36
4	38	36
6	39	32
Crude product	38	30
Plated product	38	36

and show that very little or no deuterium is lost after the first 0.5 min of the reaction.

[2-^{2}H]-2-*phenylthiohexan*-3-*one* (49). To sodium hydride (12 mg, 0.5 mmol) was added a solution of 2-phenylthiohexan-3-one (16; R^1 = Me, R^2 = Pr^n) (79 mg, 0.25 mmol) in THF (5 ml) and the mixture stirred for 15 min at room temperature. After heating under reflux for 5 min, the mixture was cooled to room temperature and deuterium oxide (0.05 ml) added. After 30 min, saturated ammonium chloride (10 ml) was added, the mixture extracted with ether (3 × 5 ml), the extract washed with water (2 × 5 ml), dried ($MgSO_4$), and evaporated to give the deuteriated *ketone* (73 mg, 92%) as an oil, R_F (CH_2Cl_2) 0.54, $\nu_{max.}$ (liq) 1 700 (C=O) and 1 578 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.1 (5 H, m, SPh), 2.58 (2 H, dt, *J* 3 and 7 Hz, CH_2CH_2CO), 1.60 (2 H, sext, *J* 7 Hz, CH_2CH_2Me), 1.37 (3 H, s, CD*Me*), and 0.88 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 209 (M^+, 18%), 138 (*M* − Pr^nCO, 100), and 109 (PhS, 22) (Found: M^+, 209.0982. $C_{11}H_{14}DOS$ requires *M*, 209.098 5. Found: *M* − Pr^nCO, 138.048 8. C_8H_8DS requires 138.048 8.

Reaction of the α-(*phenylthio*)*ketone* (49) *with* TsOH. To a solution of the ketone (49) (31 mg, 0.15 mmol) heated under reflux in benzene (3 ml) and benzenethiol (20 mg, 0.18 mmol) was added toluene-*p*-sulphonic acid (30 mg, 0.16 mmol). After 5 min, work-up as before gave the ketone (29 mg, 94%). Mass spectrometry showed 72% retention of deuterium at the 2-position.

Other Reactions of Adducts (14) *and* (19) *with* TsOH.—*Reaction of* 1-*phenyl*-2,2-*bis*(*phenylthio*)*butan*-1-*ol*. In a similar way the alcohol (14; R^1 = Et, R^2 = Ph) (110 mg, 0.30 mmol) and toluene-*p*-sulphonic acid (60 mg, 0.32 mmol) gave, after 5 min, an oil. This gave two components (R_F 0.6 and 0.8) on preparative t.l.c. (CH_2Cl_2) which were

* This compound has been prepared from the corresponding α-halo-ketone, see ref. 57.

not identified. The corresponding deuteriated alcohol (19; R^1 = Et, R^2 = Ph, R^3 = D) also gave unidentified products.

Reaction of 2,2-*bis*(*phenylthio*)*butan*-1-*ol*. Toluene-*p*-sulphonic acid (132 mg, 0.7 mmol) was added to the alcohol (14; R^1 = Et, R^2 = R^3 = H) (136 mg, 0.47 mmol) heated under reflux in benzene (10 ml). After 11 min, the solution was cooled, poured into saturated sodium carbonate (20 ml), extracted with ether (3 × 10 ml), the extract washed with water (2 × 10 ml), dried ($MgSO_4$), and evaporated to give an oil, which was purified by preparative t.l.c. to give 1-phenylthiobutan-2-one (37 mg, 44%), identical with that prepared previously.

1-[1-(*Phenylthio*)*cyclohexyl*]*propanone* (52).—Similarly the alcohol (19; R^1 = Et, R^2R^3 = $[CH_2]^5$) (115 mg, 0.31 mmol) and toluene-*p*-sulphonic acid (70 mg, 0.37 mmol) gave the α-(*phenylthio*)*ketone* (33 mg, 41%) as an oil, R_F (CH_2Cl_2) 0.8, $\nu_{max.}$ (liq) 1 706 (C=O) and 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.5—7.0 (5 H, m, SPh), 2.9—2.2 (2 H, m, CH_2Me), 2.2—1.2 (10 H, m, cyclohexyl), and 1.03 (3 H, dt, *J* 2.5 and 7 Hz, CH_2*Me*), *m/e* 248 (M^+, 65%), 191 (*M* − EtCO, 7), 139 (*M* − SPh, 22), 110 (PhSH, 72), 81 (cyclohexenyl, 35), and 57 (EtCO, 100) (Found: M^+, 248.125 2. $C_{15}H_{20}OS$ requires *M*, 248.123 4).

Reaction of Alcohols (53) *and* (54) *with* TsOH.—Treatment of these alcohols in a similar way gave only mixtures of unidentified products.

1-*Ethyl*-3-*methyl*-2-(*phenylthio*)*indene* (56).—Toluene-*p*-sulphonic acid (120 mg, 0.63 mmol) was added to the alcohol (55 or 14, R^1 = Pr^n, R^2 = Ph, R^3 = Me) (145 mg, 0.37 mmol) heated under reflux in benzene (10 ml). After 10 min, the solution was cooled, poured into saturated sodium carbonate (20 ml), extracted with ether (3 × 10 ml), the extract washed with water (2 × 10 ml), dried ($MgSO_4$), and evaporated to give an oil, which was purified by preparative t.l.c. to give the *indene* (56 mg, 57%) as an oil, R_F (CCl_4) 0.55, $\nu_{max.}$ (liq) 1 580 cm^{-1} (PhS), δ($CDCl_3$) 7.7—7.1 (9 H, m, Ph and C_6H_4), 3.72—3.5 (1 H, m, C*H*CH_2 *), 2.37 (3 H, d, *J* 2 Hz, C=CMe *), 2.3—1.7 (2 H, m, CHCH_2*Me), and 0.68 (3 H, t, *J* 7.5 Hz, CH_2*Me*), *m/e* 266 (M^+, 30%), 157 (*M* − SPh, 100), and 142 (*M* − SPh − Me, 53) (Found: M^+, 266.112 5. $C_{18}H_{18}S$ requires *M*, 266.112 8).

[8/689 *Received*, 12*th April*, 1978]

* Shows homoallylic splitting.

REFERENCES

[1] Preliminary communications: (*a*) P. Blatcher, J. I. Grayson, and S. Warren, *J.C.S. Chem. Comm.*, 1976, 547; (*b*) P. Blatcher and S. Warren, *ibid.*, p. 1055.

[2] A. T. Nielsen and W. J. Houlihan, ' Organic Reactions,' Wiley, New York, 1968, vol. 16, ' The Aldol Condensation '; H. O. House, ' Modern Synthetic Reactions,' Benjamin, Menlo Park, 1972, 2nd edn., pp. 492—785.

[3] A. H. Davidson, P. K. G. Hodgson, D. Howells, and S. Warren, *Chem. and Ind.*, 1975, 455.

[4] A. Lapworth and R. H. F. Manske, *J. Chem. Soc.*, 1928, 2533; M. Saltzman, *J. Chem. Educ.*, 1972, **49**, 750.

[5] D. Seebach and M. Kolb, *Chem. and Ind.*, 1974, 687.

[6] J. D'Angelo, *Tetrahedron*, 1976, **32**, 2979.

[7] J. Szmuszkovicz, *Adv. Org. Chem.*, 1963, **4**, 1; P. Hickmott and Suschitzky, *Chem. and Ind.*, 1970, 1188; M. E. Kuehne, *Synthesis*, 1970, 510.

[8] G. Stork and P. F. Hudrlik, *J. Amer. Chem. Soc.*, 1968, **90**, 4462.

[9] R. K. Boeckman, *J. Amer. Chem. Soc.*, 1974, **96**, 6179; G. Stork and J. Singh, *ibid.*, p. 6181; G. Stork and J. D'Angelo, *ibid.*, p. 7114.

[10] E. J. Corey and D. Seebach, *J. Org. Chem.*, 1966, **31**, 4097.

[11] E. J. Corey and D. Seebach, *Angew. Chem. Internat. Edn.*, 1965, **4**, 1075, 1077; D. Seebach, *ibid.*, 1969, **8**, 639; *Synthesis*, 1969, 17.

[12] B.-T. Gröbel and D. Seebach, *Synthesis*, 1977, 357.

[13] O. W. Lever, *Tetrahedron*, 1976, **32**, 1943.

[14] D. Seebach and D. Steinmüller, *Angew. Chem. Internat. Edn.*, 1968, **7**, 619; D. Seebach, D. Steinmüller, and F. Demuth, *ibid.*, p. 620.

[15] R. B. Woodward, I. J. Pachter, and M. L. Scheinbaum, *J. Org. Chem.*, 1971, **36**, 1137; K. Narasaka, T. Sakashita, and T. Mukaiyama, *Bull. Chem. Soc. Japan*, 1972, **45**, 3724; T. Oishi, K. Kamemoto, and Y. Ban, *Tetrahedron Letters*, 1972, 1085; M. Fetizon and M. Jurion, *J.C.S. Chem. Comm.*, 1972, 382; M. Hojo and R. Masuda, *Synthesis*, 1976, 678; M. Muxfedlt, W.-D. Unterweger, and G. Helmchen, *ibid.*, *p.* 694.

[16] S. Rozan, I. Shahak, and E. D. Bergmann, *Tetrahedron Letters*, 1972, 1837; K. Mori, H. Hashimoto, Y. Takenaka, and T. Takigawa, *Synthesis*, 1975, 726; R. D. Balamson, V. M. Kobal, and R. R. Schumacher, *J. Org. Chem.*, 1977, **42**, 393.

[17] J. F. Arens, M. Fröling, and A. Fröling, *Rec. Trav. chim.*, 1959, **78**, 663; A. Fröling and J. F. Arens, *Rec. Trav. chim.*, 1962, **81**, 1009.

[18] W. E. Truce and F. E. Roberts, *J. Org. Chem.*, 1963, **28**, 961.

[19] T. Mukaiyama, K. Narasaka, and M. Furusato, *J. Amer. Chem. Soc.*, 1972, **94**, 8641.

[20] G. Schill and C. Merkel, *Synthesis*, 1975, 387.

[21] T. Cohen, D. Kuhn, and J. R. Falck, *J. Amer. Chem. Soc.*, 1975, **97**, 4749.

[22] M. L. Wolform, *J. Amer. Chem. Soc.*, 1929, **51**, 2188; F. Weygand, H. J. Bestmann, and H. Ziemann, *Chem. Ber.*, 1958, **91**, 1040; F. Weygand, H. J. Bestmann, H. Ziemann, and E. Klieger, *ibid.*, p. 1043; R. J. Cregge, J. L. Herrmann, J. E. Richman, R. F. Romanet, and R. H. Schlessinger, *Tetrahedron Letters*, 1973, 2595, 2599, 2603; L. M. Lerner *J. Org. Chem.*, 1976, **41**, 2228.

[23] K. Ogura and G. Tsuchihashi, *Tetrahedron Letters*, 1971, 3151; 1972, 1383; J. E. Richman, J. L. Herrmann, and R. H. Schlessinger, *ibid.*, 1973, 3267, 3271, 3275; G. Schill and P. Jones, *Synthesis*, 1974, 117.

[24] R. A. Ellison and W. D. Woessner, *J.C.S. Chem. Comm.*, 1972, 529; E. Hunt and B. Lythgoe, *ibid.*, p. 757; E. W. Colvin, T. A. Purcell, and R. A. Raphael, *ibid.*, p. 1031; E. J. Corey and M. G. Bock, *Tetrahedron Letters*, 1975, 2643.

[25] P. Brownbridge and S. Warren, *J.C.S. Chem. Comm.*, 1975, 820; *J.C.S. Perkin I*, 1976, 2125; 1977, 1131; 2272; P. Brownbridge, I. Fleming, A. Pearce, and S. Warren, *J.C.S. Chem. Comm.*, 1976, 751.

[26] A. W. Herriott and D. Picker, *Synthesis*, 1975, 447; see also A. J. H. Labuschagne, J. S. Malherbe, C. J. Meyer, and D. F. Schneider, *Tetrahedron Letters*, 1976, 3571.

[27] T. C. Whitner and E. E. Reid, *J. Amer. Chem. Soc.*, 1921, **43**, 638.

[28] M. Fieser and L. F. Fieser, ' Reagents for Organic Synthesis,' Wiley–Interscience, New York, vol. 3, 1972, p. 337.

[29] D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 1974, **7**, 147; B. M. Trost, K. Hiroi, and S. Kurozumi, *J. Amer. Chem. Soc.*, 1975, **97**, 438; B. M. Trost and K. Hiroi, *ibid.*, p. 6911.

[30] D. F. Tavares and R. E. Estep, *Tetrahedron Letters*, 1973, 1229.

[31] J. I. Grayson and S. Warren, *J.C.S. Perkin I*, 1977, 2263.

[32] R. C. Cookson and P. J. Parsons, *J.C.S. Chem. Comm.*, 1976 990.

[33] N. Kharasch, W. King, and T. C. Bruice, *J. Amer. Chem. Soc.*, 1955, **77**, 931; N. Kharasch in ' The Chemistry of Organo-Sulphur Compounds,' ed. N. Kharasch, Pergamon, Oxford, 1961, vol. 1, p. 392.

[34] P. Blatcher, S. Ncube, A. Pelter, K. Smith, and S. Warren, *Tetrahedron Letters*, 1978, 2349.

[35] T. Mukaiyama, M. Shiono, and T. Sato, *Chem. Letters*, 1974, 37.

[36] A. H. Davidson, I. Fleming, J. I. Grayson, A. Pearce, R. L. Snowden, and S. Warren, *J.C.S. Perkin* 1, 1977, 550; A. H. Davidson, C. Earnshaw, J. I. Grayson, and S. Warren, *ibid.*, p. 1452.

[37] D. Dieterich in ' Methoden der Organischen Chemie ' (Houben-Weyl), Vol. VII 2a, ' Ketone,' ed. E. Müller, Thieme Stuttgart, 1973, pp. 950—987.

[38] D. Seebach and M. Teschner, *Chem. Ber.*, 1976, **109**, 1601; B. M. Trost, T. N. Saltzmann, and K. Hiroi, *J. Amer. Chem. Soc.*, 1976, **98**, 4887.

[39] P. Brownbridge and S. Warren, *J.C.S. Chem. Comm.*, 1977, 465.
[40] A. Deljac, Z. Stefanac, and K. Balenovic, *Tetrahedron*, 1966, *Suppl.* 8, 33.
[41] T. Cohen, G. Herman, J. R. Falck, and A. J. Mura, *J. Org. Chem.*, 1975, **40**, 812.
[42] E. Benzing, U.S.P., 3,118,002 (*Chem. Abs.*, 1964, **60**, P11899d); M. F. Shostakovskii, A. S. Atavin, B. A. Trofimov, A. V. Gusarov, and G. A. Gladkova, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1964, **9**, 1686 (*Chem. Abs.*, 1964, **61**, 15969f).
[43] E. J. Corey and J. W. Suggs, *Tetrahedron Letters*, 1975, 2647.
[44] A. R. Battersby, J. Staunton, and M. C. Summers, *J.C.S. Perkin I*, 1976, 1052.
[45] W. J. Gensler, F. Johnson, and A. D. B. Sloan, *J. Amer. Chem. Soc.*, 1960, **82**, 6074.
[46] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 1913, **103**, 1923.
[47] E. B. Ludlam, *J. Chem. Soc.*, 1902, **81**, 1189.
[48] G. A. R. Kon and J. F. Thorpe, *J. Chem. Soc.*, 1919, **115**, 703.
[49] H. Meerwein, *Annalen*, 1919, **419**, 167.
[50] S. F. Bedell, E. C. Spaeth, and J. M. Bobbitt, *J. Org. Chem.*, 1962, **27**, 2026.
[51] E. G. G. Werner, *Rec. Trav. chim.*, 1949, **68**, 509.