Hard Acid and Soft Nucleophile Systems. Part 11.[1] Hard-Soft Affinity Inversion: Dehalogenation of α-Halogeno Ketones with Aluminium Chloride and a Thiol

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α-Halogeno ketones have been dehalogenated with a combination of aluminium chloride and ethanethiol. The mechanism involved in deiodination and debromination differs from that of dechlorination and defluorination. A hard-hard interaction between carbonyl oxygen and aluminium chloride and a soft-soft interaction between iodine or bromine and thiol are the dominant factors for direct deiodination and debromination. In dechlorination and defluorination there is initial formation of the corresponding dithioacetal, whereby hard carbonyl oxygen is replaced by the soft sulphur atom. α-Chloro- and α-fluoro-dithioacetals then undergo dehalogenation to afford vinyl sulphide as a result both of a favourable soft-soft interaction between the sulphur atoms in the dithioacetal entity and thiol, and also a favourable hard-hard interaction between the nucleophilic chlorine or fluorine and aluminium chloride. α-Chloro- and α-fluoro-benzyl benzyl ketones afforded the dehalogenated product with concomitant 1,2-transposition of the carbonyl group. This suggests that there is an indirect path which operates competitively *via* a 1,2-dithio-olefin from α-halogenodithioacetals to vinyl sulphide. Addition of thiol to vinyl sulphide leads to the final product. A concept of hard-soft affinity inversion is proposed.

Systems consisting of a hard acid and a soft nucleophile have been utilized for the cleavage of a variety of chemical bonds. Aluminium chloride–ethanethiol is such a system and this has been successfully utilized for the cleavage of bonds including C–O,[2,3] C–S,[4] C–NO_2,[5] C=C,[6] and C–halogen.[7] We found that the same combination effected dehalogenation of α-halogeno ketones to give the dithioacetal of the corresponding ketones.[8] Since many practically useful methods for dehalogenation of α-halogeno ketones have been reported,[9] the present method is merely a complement from a synthetic point of view. However, as will be discussed, the mechanism involved in dechlorination and defluorination with this combination is completely different from that of debromination and deiodination.

In α-bromo or α-iodo ketones, carbonyl oxygen and halogens are regarded as a hard centre and a soft centre, respectively. Thus, a pertinent combination of a hard acid and a soft nucleophile can be used for dehalogenation of α-bromo and α-iodo ketones as shown in Figure 1. A number of systems have been developed for this type of transformation.[9] On the other hand, since chlorine and fluorine are relatively harder than bromine and iodine, a soft nucleophile will encounter greater difficulty in attacking the halogen atom. According to the hard and soft acids and bases (HASB) principle, the electron movement shown in Figure 2, the reverse of that shown in Figure 1, is expected when the hard carbonyl oxygen is replaced by sulphur which is regarded as a soft atom. Thus, the transformation of an α-chloro or α-fluoro ketone into the corresponding dithioacetal results in the reversal of hard-soft dissymmetry as well as charge dissymmetry. The details of this type of dehalogenation will be discussed in this report.

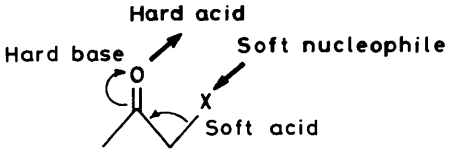


Figure 1. For deiodination and debromination

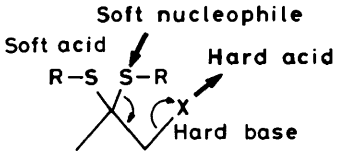
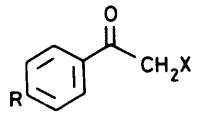


Figure 2. For dechlorination and defluorination

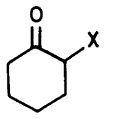
Results

All α-halogeno ketones were reductively dehalogenated by aluminium chloride–ethanethiol (Table 1): thus defluorination occurs readily (run 13, 15, 16, and 17 in Table 1). Diethyl sulphide can be used instead of ethanethiol for deiodination and debromination (run 2 and 4 in Table 1), but not for defluorination (run 14 in Table 1).

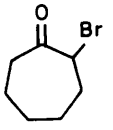
Comparison of the product distributions upon partial dehalogenation under mild conditions of α-bromoacetophenone (**2**) and α-chloro- (**8**) and α-fluoro-acetophenone (**10**) show that there is a marked difference between the last two and the first (Table 2). In these reactions the dithioacetals (**26**; X = Cl and F) formed were too unstable to be isolated in pure form, easily decomposing to provide (**14**) during the purification or under g.l.c. analysis. α-Chloro- and α-fluoro-benzyl benzyl ketones (**29**) and (**30**) again showed different behaviour from α-iodo- and α-bromo-benzyl benzyl ketones (**27**) and (**28**). Upon dehalogenation with ethanethiol as a nucleophile, (**29**) and (**30**) afforded (**34**) and (**35**), resulting from the 1,2-transposition of the carbonyl group, in 30% yield of the total products (runs 3 and 4 in Table 3). Dehalogenation of the chloro ketone (**29**) with ethanedithiol as a nucleophile provided the dithioacetal (**37**) (57%) as a result of carbonyl group migration, along with the normal product (**36**) (43%). A closely similar ratio of products was obtained when 5,6-dihydro-1,4-dithiane (**38**) was treated under the standard conditions. Dehalogenation of α-iodo- (**27**) and α-bromo-benzyl benzyl ketones (**28**) failed to give any products resulting from carbonyl group migration. This again suggests the mechanism for dehalogenation of the former halogeno ketones differs from that of the latter.



(1) R = H, X = I
(2) R = H, X = Br
(3) R = X = Br
(4) R = Ph, X = Br
(8) R = H, X = Cl
(10) R = H, X = F



(5) X = Br
(9) X = Cl



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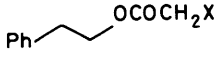
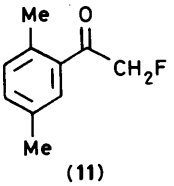


(7) X = Br
(20) X = H



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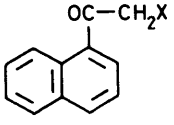
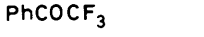


(12) X = F
(24) X = H



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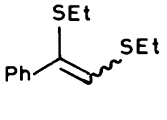

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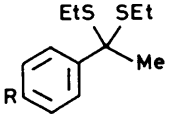
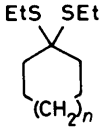
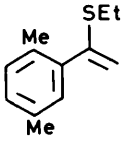


(15) R = H
(16) R = Br
(17) R = Ph



(18) n = 1
(19) n = 2



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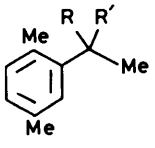
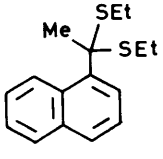


(22) R = R′ = SEt
(23) R, R′ = O



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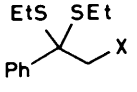

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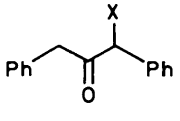
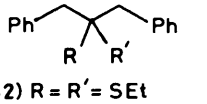
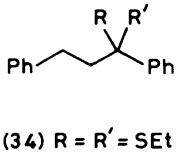


(27) X = I
(28) X = Br
(29) X = Cl
(30) X = F
(31) X = H

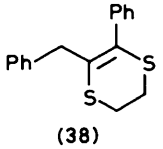


(32) R = R′ = SEt
(36) R = R′ = SCH_2CH_2S



(34) R = R′ = SEt
(37) R = R′ = SCH_2CH_2S

(33) R = SEt, R′ = H
(35) R = H, R′ = SEt



(38)

Table 1. Dehalogenation of α-halogeno ketones with aluminium chloride–ethanethiol

Run	α-Halogeno ketone	Reaction time[a] (min)	Product isolated yield (%)
1	(1)	5	PhCOMe (*ca.* 100)[b]
2	(1)	20[c]	PhCOMe (60)
3	(2)	20	(15) (98)
4	(2)	20[c]	PhCOMe (73)
5	(3)	30	(16) (86)
6	(4)	20	(17) (75)
7	(5)	15	(18) (56)
8	(6)	15	(19) (56)
9	(7)	100[d]	(20) (14)
10	(8)	10	(15) (77)
11	(8)	100[c]	PhCOMe (6)
12	(9)	15	(18) (69)
13	(10)	20	(15) (67)
14	(10)	80[c]	No reaction
15	(11)	15	(21) (53), (22) (8), (23) (11)
16	(12)	20	(24) (26), (25) (61)
17	(13)	120	(15) (57)
18	(14)	20	(15) (73)

[a] All reactions were run at 0 °C. [b] Determined by g.l.c. analysis (column, FFAP; temp. 150 ⟶ 180 °C; 1,4-dimethylnaphthalene as an internal standard). [c] Diethyl sulphide was used for ethanedithiol. [d] Aluminium bromide (3.7 mol equiv.) was used at 25 °C.

Table 2. Partial dehalogenation of α-halogenoacetophenones

Compd.	Product (%) (26)	(14)	(15)	Recovery of starting material (%)
(2)	0	4	14	54
(8)	3 (X = Cl)	53	8	18
(10)	10 (X = F)	55	6	27

Discussion

α-Iodo and α-Bromo Ketones.—The dehalogenation of α-iodo and α-bromo ketones has the following features. (i) Both ethanethiol and diethyl sulphide are effective as a nucleophile (runs 1—8 in Table 1). (ii) In the partial debromination of (**2**), the yield of the 1,2-disulphide (**14**) arising from migration of the ethylthio group is extremely low compared with the yields from (**8**) and (**10**) (Table 2). (iii) Upon dehalogenation of the α-halogeno ketones (**27**) and (**28**), there was no migration of the carbonyl group (runs 1 and 2 in Table 3). All these features indicate the direct removal of iodine or bromine in a manner as shown in Figure 1 which follows the HSAB principle or Saville's rule.[10]

α-Bromo and α-chloro ketones are known to be dehalogenated under basic conditions with thiolate ion in a two-step process *via* α-thioketones.[11] Involvement of the latter in the present systems is unlikely, since thiol can be replaced by sulphide for deiodination and debromination (runs 2 and 4 in Table 1).

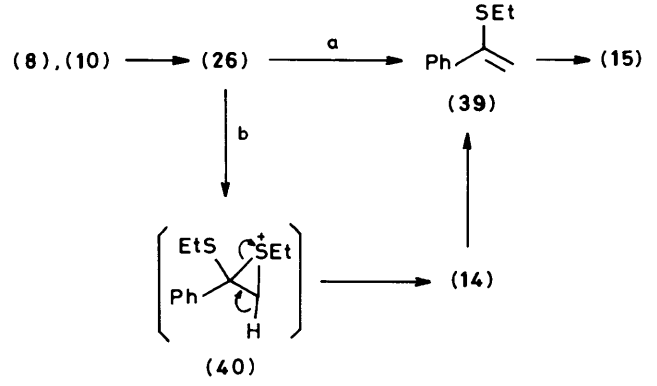
α-Chloro and α-Fluoro Ketones.—The distribution of products resulting from partial dehalogenation of α-bromoacetophenone (**2**) differed markedly from those of α-chloro- and α-fluoroacetophenones which were closely similar (Table 2). This indicated that the mechanism for deiodination and debromination differed from that of dechlorination and defluorination. α-Fluoroacetophenone (**10**) was defluorinated with ethanethiol but not with diethyl sulphide as a nucleophile (runs 13 and 14 in

Table 3. Dehalogenation of α-halogenobenzyl benzyl ketones and related reactions[a]

Run	Compd.	Thiol	Product (%)	Carbonyl migration (%)
1	(**27**)	EtSH	(**31**) (35), (**32**) (23), (**33**) (37)	0
2	(**28**)	EtSH	(**32**) (39), (**33**) (58)	0
3	(**29**)	EtSH	(**32**) (58), (**33**) (13), (**34**) (25), (**35**) (4)	29
4	(**30**)	EtSH	(**32**) (44), (**33**) (10), (**34**) (20), (**35**) (3)	30
5	(**29**)	$HSCH_2CH_2SH$	(**36**) (43), (**37**) (57)	57
6	(**38**)	$HSCH_2CH_2SH$	(**36**) (35), (**37**) (54)	61

[a] All reactions were run at 0 °C with $AlCl_3$ (1.5 mmol equiv.) for 10 min.

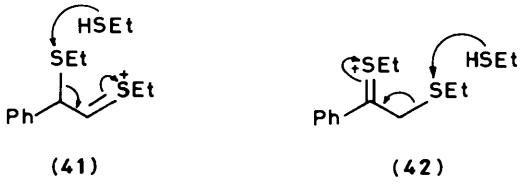
Table 1). Although dechlorination of α-chloroacetophenone (**8**) with ethanethiol furnished the dithioacetal (**15**) in a reasonable yield within 10 min (run 10 in Table 1), little acetophenone was obtained even after 100 min when diethyl sulphide was used as a nucleophile (run 11 in Table 1). The above observations indicate that initial dithioacetalization is indispensable to dechlorination and defluorination. Thus, the hard-soft affinity inversion shown in Figure 2 plays a crucial role in dehalogenation of α-chloro and α-fluoro ketones.



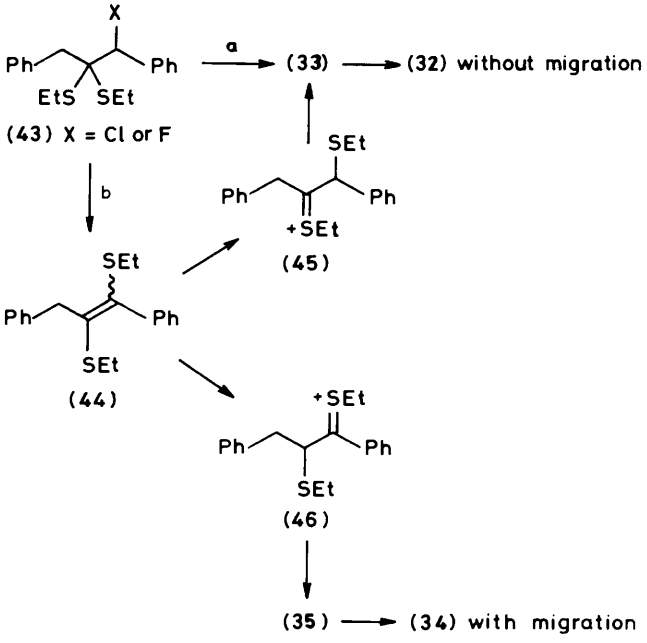
Scheme 1.

Both paths a and b in Scheme 1 operate competitively in formation of the final product from the α-halogenodithioacetals (**26**; X = Cl and F). By path a, α-halogenodithioacetals (**26**; X = Cl and F) are converted into (**39**) directly *via* the electron shift shown in Figure 2. Path b involves the formation of the intermediate sulphonium ion (**40**) as a result of anchimeric assistance by sulphur[12] followed by scission of the episulphonium ring to provide 1,2-bis(ethylthio)styrene (**14**); the latter is then converted into (**39**) under the reaction conditions. 1-Ethylthiostyrene (**39**) has been shown to furnish the dithioacetal (**15**) upon treatment with aluminium chloride–ethanethiol.[5] Although 1,2-bis(ethylthio)styrene (**14**) was obtained from the partial dehalogenation of (**8**) and (**10**) in *ca.* 55% yield (Table 2) and shown to provide the final product (**15**) under standard reaction conditions (run 18 in Table 1), its involvement as an intermediate in the process was, at this stage, unconfirmed since, α-chlorodithioacetal (**26**; X = Cl) being unstable could have given rise to it as a result of the isolation procedure. This means that path b may not operate under the reaction conditions and that (**14**) was generated as a result of the reaction being quenched halfway. To clarify this point the results in Table 3 are important.

By path b, protonation of (**14**) may take place either at C-1 or at C-2 affording the homobenzyl cation (**41**) or the benzyl cation (**42**), respectively. Because of the greater stability of the cation (**42**) over (**41**), protonation at C-2 occurred exclusively to furnish (**39**) *via* (**42**). The same consideration can be applied to



the dibenzyl ketone series. In the dehalogenation of α-chloro- or α-fluoro-benzyl benzyl ketone (**29**) or (**30**), the 1,2-bis(ethylthio)olefin (**44**) must be formed *via* the dithioacetal (**43**) if the reaction follows path b (Scheme 2). The cation (**45**) is formed by protonation at the benzylic carbon atom of (**44**), while protonation at the homobenzylic carbon generates the benzylic cation (**46**) this being more stable than (**45**). This leads to the prediction that 1,2-transposition of the carbonyl group will occur to some extent when (**29**) and (**30**) are dehalogenated. In fact, both the α-chloro ketone (**29**) and the α-fluoro ketone (**30**) afforded products (30%), (**34**) + (**35**), resulting from carbonyl group migration (runs 3 and 4 in Table 3); this confirmed the existence of the path b.



Scheme 2.

Hard-Soft Affinity Inversion.—Except for bonds such as symmetrically substituted carbon–carbon bonds, all chemical bonds are inherently disymmetric in two respects: one of them is their charge dissymmetry. Reversal of the latter by modifying the structural unit has been called umpolung[13] and has become

one of heuristic principles in synthetic organic chemistry.[14] In contrast, reversal of hard-soft dissymmetry has received scant attention: thus conversion of a hard centre into a soft centre by modifying the structural unit may be called *hard-soft affinity inversion*. Dechlorination and defluorination of α-chloro and α-fluoro ketones with aluminium chloride and ethanethiol illustrates the usefulness of this concept.

In the dehalogenation of α-iodo and α-bromo ketones with aluminium chloride and ethanethiol, a favourable hard-hard interaction between the carbonyl oxygen and aluminium chloride and a favourable soft-soft interaction between iodine or bromine and ethanethiol are main driving forces for dehalogenation. On the other hand, a soft-soft interaction cannot be expected for α-chloro and α-fluoro ketones, because electrophilic chlorine and fluorine are harder than electrophilic iodine and bromine. Thus, in the dechlorination and the defluorination, dithioacetal must be formed initially, whereby the hard oxygen atom is replaced by the soft sulphur atom to introduce a favourable soft-soft interaction which cannot operate in the parent compound.

Experimental

M.p.s were determined with a Yanagimoto micro apparatus and are uncorrected. I.r. spectra were recorded with a JASCO A-202 spectrophotometer. ^{1}H N.m.r. spectra were measured in $CDCl_3$ solution with a JEOL JNM-PMX 60 spectrometer or a JEOL JNM-FX 100 spectrometer, and chemical shifts are reported in p.p.m. relative to internal $SiMe_4$. High-resolution mass spectra were determined on a JEOL JMS-DX 300 mass spectrometer. G.l.c. analyses were performed on a Shimazu Model GC-4CM chromatograph.

Materials.—α-Halogeno ketones (**2**), (**3**), (**4**), (**8**), (**9**), and (**13**) are commercially available. α-Halogeno ketones (**1**),[15] (**5**),[16] (**6**),[16] (**10**),[17] (**28**),[18] and (**29**)[19] are known compounds.

Phenethyl Bromoacetate (**7**).—To an ice-cooled solution of phenethyl alcohol (5.03 g, 41 mmol) and triethylamine (6.2 ml, 44 mmol) in chloroform (500 ml) under nitrogen was added dropwise bromoacetyl bromide (4.3 ml, 49 mmol), followed by 4-dimethylaminopyridine (1.02 g, 8.4 mmol). After being stirred at room temperature for 2 h, the reaction mixture was poured into ice–water, and the mixture was extracted with ether. The ether solution was shaken with dilute HCl, and the organic layer was washed with aqueous Na_2CO_3 and brine and dried (Na_2SO_4). The crude product was distilled *in vacuo* to give (**7**) (3.75 g, 37%) as a colourless oil, b.p. 110—112 °C (0.7 Torr); δ 2.97 (2 H, t, *J* 7 Hz), 3.77 (2 H, s), 4.36 (2 H, t, *J* 7 Hz), and 7.22 (5 H, s); $\nu_{max.}$($CHCl_3$) 3 030, 1 735, 1 600, 1 500, and 1 280 cm^{-1} (Found: C, 49.8; H, 4.6. $C_{10}H_{11}BrO_2$ requires C, 49.40; H, 4.56%).

2-Fluoro-2′,5′-dimethylacetophenone (**11**).—This compound was prepared from *p*-xylene in 18% yield by the method of Bergmann and Kalmus:[17] it formed colourless crystals from MeOH, m.p. 39—39.5 °C; δ 2.35 (3 H, s), 2.47 (3 H, s), 5.30 (2 H, d, *J* 46 Hz), and 7.1—7.4 (3 H, m); $\nu_{max.}$($CHCl_3$) 1 700 and 1 090 cm^{-1} (Found: M^+, 166.0794. $C_{10}H_{11}FO$ requires *M*, 166.0793).

2-Fluoro-1′-acetonaphthone (**12**).—This compound was prepared from naphthalene in 3% yield by the method of Bergmann and Kalmus:[17] it had m.p. 82—84 °C; δ 5.65 (2 H, d, *J* 46 Hz), 7.6 (2 H, m), 7.95 (4 H, m), 8.4 (1 H, br s); $\nu_{max.}$($CHCl_3$) 1 700 cm^{-1} (Found: M^+, 188.0646. $C_{12}H_9FO$ requires *M*, 188.0637).

Benzyl α-Iodobenzyl Ketone (**27**).—This compound was prepared from the trimethylsilyl enol ether of dibenzyl ketone (**31**) in 41% yield by the method of Motohashi and Satomi:[20] it formed pale yellow needles from Et_2O, m.p. 83.3—83.7 °C; δ 3.95 (2 H, d, *J* 3 Hz), 5.74 (1 H, s), and 7.0—7.5 (10 H, m); $\nu_{max.}$($CHCl_3$) 1 700, 1 480, and 1 430 cm^{-1} (Found: C, 53.7; H, 3.95. $C_{15}H_{13}IO$ requires C, 53.6; H, 3.9%).

Benzyl α-Fluorobenzyl Ketone (**30**).—This compound was prepared from (**29**) in 6% yield by the method of Tannhauser, *et al.*:[21] it formed colourless needles from acetone–hexane, m.p. 51.5—53 °C; δ 3.82, 3.87 (2 H, each s), 5.75 (1 H, d, *J* 48 Hz), 6.9—7.4 (5 H, m), and 7.34 (5 H, s); $\nu_{max.}$($CHCl_3$) 3 030, 1 730, 1 600, 1 500, and 1 450 cm^{-1} (Found: M^+, 228.0946. $C_{15}H_{13}FO$ requires *M*, 228.0950).

General Procedure for Dehalogenation of α-Halogeno Ketones (*Table 1*).—To a stirred and ice-cooled solution of the α-halogeno ketone (1 mmol) in dry dichloromethane (2 ml, MeOH-free) under nitrogen were added aluminium chloride (1.5 mmol) and ethanethiol or diethyl sulphide (0.4 ml). After being stirred under the conditions described in Table 1, the reaction mixture was poured into ice–water, and the mixture was extracted with dichloromethane. The organic layer was shaken with brine, dried (Na_2SO_4), filtered, and then evaporated to leave a crude material, which was purified by column chromatography or preparative t.l.c. over silica gel. The dithioacetals (**15**)[22] and (**18**)[6b] are known compounds.

Dithioacetal (**16**). A colourless oil; δ 1.15 (6 H, t, *J* 8 Hz), 1.97 (3 H, s), 2.50 (4 H, q, *J* 8 Hz), 7.35 (2 H, AB d, *J* 10 Hz), and 7.54 (2 H, AB d, *J* 10 Hz); $\nu_{max.}$($CHCl_3$) 2 980, 1 580, 1 485, and 1 200 cm^{-1} (Found: C, 46.85; H, 5.75. $C_{12}H_{17}BrS_2$ requires C, 47.21; H, 5.61%).

Dithioacetal (**17**). Colourless oil; δ 1.17 (6 H, t, *J* 8 Hz), 2.04 (3 H, s), 2.54 (4 H, q, *J* 8 Hz), and 7.2—7.8 (9 H, m); $\nu_{max.}$($CHCl_3$) 2 990, 1 600, 1 580, 1 485, and 1 195 cm^{-1} (Found: C, 71.8; H, 7.35. $C_{18}H_{22}S_2$ requires C, 71.47; H, 7.33%).

Dithioacetal (**19**). Colourless oil; δ 1.22 (6 H, t, *J* 7 Hz), 1.4—2.1 (12 H, m), and 2.57 (4 H, q, *J* 7 Hz); $\nu_{max.}$($CHCl_3$) 2 935 and 1 450 cm^{-1} (Found: C, 60.8; H, 10.4. $C_{11}H_{22}S_2$ requires C, 60.48; H, 10.15%).

Compounds (**21**) *and* (**23**). The structures of these compounds were established on the basis of the following ^{1}H n.m.r. data and were confirmed by the fact that (**21**) and (**23**) were converted into the dithioacetal (**21**) by the treatment with BF_3·OEt_2–EtSH. Compound (**21**): δ 1.25 (3 H, t, *J* 7 Hz), 2.31 (6 H, s), 2.66 (2 H, q, *J* 7 Hz), 5.05 (1 H, s), 5.15 (1 H, s), and 7.01 (3 H, s); compound (**23**): δ 2.34 (3 H, s), 2.46 (3 H, s), 2.54 (3 H, s), 7.1 (2 H, br s), and 7.4 (1 H, br s).

Dithioacetal (**22**). Colourless oil; δ 1.13 (6 H, t, *J* 8 Hz), 2.15 (3 H, s), 2.30 (3 H, s), 2.47 (4 H, q, *J* 8 Hz), 2.71 (3 H, s), 7.0 (2 H, br s), and 7.4 (1 H, br s); $\nu_{max.}$($CHCl_3$) 2 990, 1 610, 1 500, 1 450, 1 375, and 1 260 cm^{-1} (Found: C, 66.25; H, 8.9. $C_{14}H_{22}S_2$ requires C, 66.08; H, 8.72%)

Dithioacetal (**25**). Pale yellow oil; δ 1.16 (6 H, t, *J* 7 Hz), 2.10 (3 H, s), 2.51 (4 H, q, *J* 7 Hz), 7.1—7.9 (6 H, m), and 7.93 (1 H, br s); $\nu_{max.}$($CHCl_3$) 1 600, 1 510, 1 445, and 1 260 cm^{-1} (Found: M^+, 276.0994. $C_{16}H_{20}S_2$ requires *M*, 276.1006).

Partial Dehalogenation (*Table 2*).—To a stirred and ice-cooled solution of the α-halogenoacetophenone (**2**), (**8**), or (**10**) (5 mmol) in dry dichloromethane (10 ml) under nitrogen were added aluminium chloride (1.6 mmol) and ethanethiol (0.75 ml). After being stirred for 5 min, the reaction mixture was treated as described in the general procedure. The yield of (**15**) and the amount of starting material recovered (Table 2) were calculated from g.l.c. analysis of the product mixture. G.l.c. analyses were performed with a 10% FFAP on Chromosorb W (AW) (3 mm × 1 m) at 180 °C with 1,4-dimethylnaphthalene as an internal standard.

Although compounds (**26**; X = F or Cl) could not be isolated

on account of their rapid transformation into (**14**) during purification or g.l.c. analysis, their existence in the product mixture was confirmed by the characteristic ^{1}H n.m.r. signal (X = F: δ 4.82, d, *J* 46 Hz; X = Cl: δ 4.07, s) and by the molecular ion peak in the high-resolution mass spectrum (X = F: Found: M^+, 244.0785. $C_{12}H_{17}FS_2$ requires *M*, 244.0756) of the mixture.

1,2-*Bis*(*ethylthio*)*styrene* (**14**). Colourless oil; δ 1.13, 1.15 (each 3 H, t, *J* 7 Hz), 1.29, 1.37 (each 3 H, t, *J* 7 Hz), 2.43, 2.53 (each 2 H, q, *J* 7 Hz), 2.71, 2.84 (each 2 H, q, *J* 7 Hz), 6.57, 6.58 (each 1 H, s), and 7.1—7.5 (5 H, m); $\nu_{max.}$(neat) 2 975, 1 595, 1 550, 1 490, and 1 440 cm^{-1} (Found: C, 63.9; H, 7.25. $C_{12}H_{16}S_2$ requires C, 64.23; N, 7.19%).

Dehalogenation of α-Halogenobenzyl Benzyl Ketones (**27**)—(**30**): *With Ethanethiol.*—α-Halogenobenzyl benzyl ketones (0.2—0.6 mmol scale) were dehalogenated according to the general procedure. The residue was separated by preparative t.l.c. (SiO_2, 15% CH_2Cl_2–hexane) to give (**31**)—(**35**).

Compound (**32**). Colourless oil; δ 1.14 (6 H, t, *J* 8 Hz), 2.37 (4 H, q, *J* 8 Hz), 3.08 (4 H, s), 7.0—7.4 (10 H, m); $\nu_{max.}$($CHCl_3$) 2 940, 1 600, 1 500, 1 450, and 1 260 cm^{-1} (Found: M^+, 316.1343. $C_{19}H_{24}S_2$ requires *M*, 316.1320).

Compound (**33**). Colourless oil; δ 1.15, 1.30 (each 3 H, t, *J* 6 Hz), 2.67, 2.80 (each 2 H, q, *J* 7 Hz), 3.77, 3.83 (each 2 H, s), 6.55 (1 H, s), 7.0—7.6 (10 H, m); $\nu_{max.}$($CHCl_3$) 3 020, 1 600, 1 495, and 1 445 cm^{-1} (Found: M^+, 254.1116. $C_{17}H_{18}S$ requires *M*, 254.1128).

Compound (**34**). Colourless oil; δ 1.19 (6 H, t, *J* 7 Hz), 2.2—2.7 (8 H, m), 6.9—7.4 (8 H, m), and 7.6—7.8 (2 H, m); $\nu_{max.}$($CHCl_3$) 2 945, 1 600, 1 495, 1 440, and 1 260 cm^{-1} (Found: M^+, 316.1325. $C_{19}H_{24}S_2$ requires *M*, 316.1320).

Compound (**35**). Colourless oil; δ 1.10 (3 H, t, *J* 7 Hz), 2.43 (2 H, q, *J* 7 Hz), 3.84 (2 H, d, *J* 7 Hz), 6.16 (1 H, t, *J* 7 Hz), 7.1—7.6 (10 H m); $\nu_{max.}$($CHCl_3$) 2 940, 1 670, 1 600, 1 495, and 1 450 cm^{-1} (Found: M^+, 254.1128. $C_{17}H_{18}S$ requires *M*, 254.1128).

Compounds (**36**) *and* (**37**). To a stirred and ice-cold solution of the substrates (**29**) and (**38**) (0.4 mmol) in dry dichloromethane (1 ml) under nitrogen were added ethanedithiol (0.2 ml) and aluminium chloride (0.6 mmol). After being stirred for 10 min, the reaction mixture was treated in the same way as general procedure. The residue was separated by preparative t.l.c. (SiO_2, 15% CH_2Cl_2–hexane) to give the dithioacetals (**36**) and (**37**).

Dithioacetal (**36**). Colourless needles from Et_2O–hexane, m.p. 55.5—56.5 °C; δ 2.75 (4 H, s), 3.24 (4 H, s), 7.1—7.5 (10 H, m); $\nu_{max.}$($CHCl_3$) 2 930, 1 600, 1 500, and 1 450 cm^{-1} (Found: M^+, 286.0887. $C_{17}H_{18}S_2$ requires *M*, 286.0850).

Dithioacetal (**37**). Colourless oil; δ 2.62 (4 H, s), 3.2—3.5 (4 H, A_2B_2), 7.0—7.4 (8 H, m), and 7.6—7.8 (2 H, m); $\nu_{max.}$($CHCl_3$) 2 930, 1 600, 1 500, 1 440, and 1 260 cm^{-1} (Found: M^+, 286.0834. $C_{17}H_{18}S_2$ requires *M*, 286.0850).

5,6-*Dihydro*-1,4-*dithiane* (**38**).—To a solution of benzyl α-chlorobenzyl ketone (**29**) (256 mg) in dry dichloromethane (2 ml) were added ethanedithiol (92 mg) and boron trifluoride–diethyl ether (135 mg) at 0 °C under nitrogen. After being stirred for 20 min, the reaction mixture was worked up and the residue was chromatographed over silica gel with 5% acetone–hexane to afford (**38**) (123 mg, 41%): colourless needles from EtOH, m.p. 98—99 °C; δ 3.26 (4 H, s), 3.50 (2 H, s), 7.0—7.4 (5 H, m), and 7.30 (5 H, s); $\nu_{max.}$($CHCl_3$) 3 005, 1 600, 1 500, and 1 450 cm^{-1} (Found: M^+, 284.0680. $C_{17}H_{16}S_2$ requires *M*, 284.0693).

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