Reduction of β-Arylthio- or β-Alkylthio-αβ-Unsaturated Ketones

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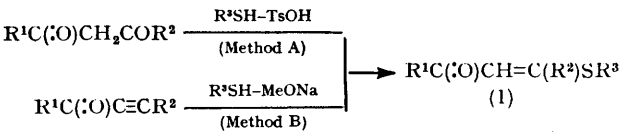
The preparation and reduction of β-arylthio- or β-alkylthio-αβ-unsaturated ketones (1) with lithium aluminium hydride or sodium borohydride have been examined. Reduction of the ketones (1) with lithium aluminium hydride gave αβ-unsaturated ketones (2), in which the olefinic (R^1) and carbonyl (R^2) substituents are reversed compared with the starting αβ-unsaturated ketone (1), or the saturated γ-hydroxy-sulphides (3). Reduction of the ketones (1) with sodium borohydride afforded only the αβ-unsaturated ketones (2). Reduction of (1) with sodium borohydride in the presence of metal halides gave the saturated ketones (5).

β-HETEROATOM substituted αβ-unsaturated ketones (β-amino, β-alkoxy, and β-arylthio- or β alkylthio-αβ-unsaturated ketones) are useful intermediates for the synthesis of heterocycles [1] and for a variety of transformation.[2] Reports on the reduction of β-amino-αβ-unsaturated ketones with aluminium hydride [3] or sodium borohydride–iron(III) chloride,[4] and β-alkoxy-αβ-unsaturated ketones with lithium aluminium hydride [5] have led us to study the chemistry of β-arylthio- or β-alkylthio-αβ-unsaturated ketones (1). Generally the regiospecific reduction (1,2- or 1,4-reduction) of αβ-unsaturated carbonyl compounds is an important reaction bcause of its utility, but it is difficult to carry out. Recently the action of hydride reducing reagents such as $LiAlH_4$ and $NaBH_4$ in conjunction with metal halides has been examined and found to afford selective reduction of αβ-unsaturated carbonyl compounds.[6] We now report the preparation and reduction of β-arylthio- or β-alkylthio-αβ-unsaturated ketones with $LiAlH_4$, $NaBH_4$, and $NaBH_4$ in the presence of metal halides.

RESULTS AND DISCUSSION

Preparation of β-Arylthio- or β-Alkylthio-αβ-Unsaturated Ketones (1).—The ketones (1) were prepared by the acid-catalysed condensation of β-diketones with the appropriate thiol (method A),[7] or the nucleophilic addition of thiolate anion to acetylenic ketones (method B) [8] (Scheme 1). Under the conditions of method (A) or

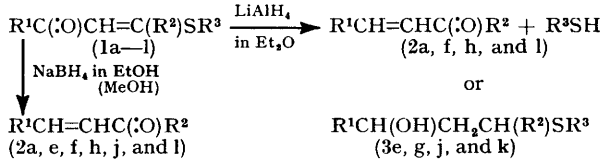


SCHEME 1

	R^1	R^2	R^3		R^1	R^2	R^3
a;	Ph	Me	Et	g;	Ph	H	Ph
b;	Ph	Me	Pr^n	h;	Me	Me	Bu^n
c;	Ph	Me	CH_2Ph	i;	Me	Me	Ph
d;	Ph	Me	Ph	j;	Me	Ph	Et
e;	Ph	Ph	Et	k;	Me	Ph	Ph
f;	Ph	H	Et	l;	$-[CH_2]_2-$		Et

(B), the ketones (1a—d, f, g, i, and j) formed are composed of a mixture of *E*- and *Z*-isomer whereas the ketones (1e, h, k, and l) are a single stereoisomer, either the *E*- or the *Z*-isomer. The pure *E*- and *Z*-isomers of (1a) and (1b) were separated by silica-gel column chromatography (eluant: benzene),† and their structures confirmed by the usual spectroscopic analysis and their behaviour upon u.v. irradiation.[9] The *E*-isomers of (1a) and (1b) isomerize to the *Z*-isomers on u.v. irradiation, and these are converted back into the *E*-isomer on heating. ^1H and ^{13}C N.m.r. data for the ketones (1) are summarized in Table 1.

Reduction of β-Arylthio- or β-Alkylthio-αβ-Unsaturated Ketones (1) *with Lithium Aluminium Hydride or Sodium Borohydride.*—When 3-ethylthio-1-phenylbut-2-en-1-one (1a) was reduced with $LiAlH_4$ in dry ether and the mixture then decomposed under acidic conditions, 4-phenylbut-3-en-2-one (2a), which has reversed substituents (Ph, Me) compared with (1a), was obtained in 94.5% yield. Similarly, reduction of (1b—d, f, h, i, and l) with $LiAlH_4$ also gave the αβ-unsaturated ketones (2a, f, h, and l) in moderate yields. However, reduction



SCHEME 2

of the ketones (1e, g, j, k) with $LiAlH_4$ under the same conditions gave the saturated γ-hydroxy-sulphides (3e, g, j, k) in high yields (Scheme 2).

On reduction with $NaBH_4$ in ethanol or methanol and treatment with acid, the ketones (1a, c—e, and g—l) gave the corresponding ketones (2a, e, f, h, j, and l) with the R^1 and R^2 substituents reversed in 14.5—69.0% yields. The αβ-unsaturated ketones (2a, e, f, h, j, and l) were identified by direct comparison of their spectral data with those of authentic samples whereas the saturated γ-hydroxy-sulphides (3e, g, j, k) were identified from their spectral data and elemental analyses. Table 2 summarizes the yields of the reduction products (2) and (3). The ketones (2) are formed by hydrolysis of a hemi-

† We previously reported that the ketones (1a, b, f, and g), which were chromatographed on a silica-gel column with benzene as eluant, followed by distillation or recrystallisation, were composed of a single stereoisomer (ref. 9). We have now reinvestigated the stereoisomers of (1), following purification simply by distillation or recrystallisation, in detail by ^1H and ^{13}C n.m.r. spectroscopy.

thioacetal formed by allylic rearrangement of the allylic alcohol (4), which is formed by selective reduction (1,2-reduction) of the carbonyl group. Attempts to isolate the intermediates (4) were unsuccessful owing to their sensitivity to moisture and acid.[5a] The saturated γ-hydroxy-sulphides (3) are presumed to arise from the 1,2-reduction of intermediate γ-oxo-sulphides, formed by 1,4-reduction of (1) followed by ketonization. The overall transformation of the ketones (1) to the ketones (2) and (3) is outlined in Scheme 3. The results in Table 2 show that $NABH_4$ is superior to $LiAlH_4$ for the selective (1,2-) reduction of the carbonyl group of (1). However, $NaBH_4$ is less reactive than $LiAlH_4$.

Reduction of the Ketones (1) *with Sodium Borohydride in the Presence of Metal Halides.*—A number of metal halides and hydride reducing reagents, such as $NaBH_4$ and $LiAlH_4$, which are claimed to give selective (1,2- or 1,4-) reduction products have been investigated recently.[10] We investigated the application of these systems to the reduction of the ketones (1). Reduction of the ethylthiobutenone (1a) with $NaBH_4$ in the presence of cerium(III) chloride ($CeCl_3 \cdot 7H_2O$) in methanol and followed by decomposition under acidic conditions gave 4-phenylbut-3-en-1-one (2a) in 78% yield. Similar reduction of the ketones (1d—f) with $NaBH_4$ in the presence of $CeCl_3 \cdot 7H_2O$ gave the ketones (2a, e, f) in 50.5—59.5% yields (Table 3). These results are similar to those for the reduction of (1) with $NaBH_4$, but the yields of (2) are slightly higher than those for the reduction of (1) with $NaBH_4$ alone. In contrast, reduction

TABLE 1

^1H and ^{13}C N.m.r. spectra of β-arylthio- or β-alkylthio-αβ-unsaturated ketones (1)

	Method	*E*/*Z* ratio [a]	^1H N.m.r. (δ in $CDCl_3$) [b]	^{13}C N.m.r. (p.p.m. in $CDCl_3$) [c,d] Carbonyl	α-Olefinic	β-Olefinic	Aliphatic	
(1a)	A	63/37	1.39, t [1.34, t] (3 H); 2.51, d, *J* 1.1 [2.39, d, *J* 1.1] (3 H); 2.93, q [2.92, q] (2 H); 6.63br, s [6.86, d, *J* 1.1] (1 H); 7.4—7.55, m (3 H); 7.85—8.0, m (2 H)	187.8 (s) [188.1, s]	113.4 (d) [116.6, d]	161.2 (s) [162.0, s]	25.8 (t) [24.8, t] 12.7 (q) [13.9, q]	21.9 (q) [24.8, q]
(1b)	A	67/33	1.07, t [1.06, t] (3 H); 1.55—1.90, m, 2 H; 2.51, d, *J* 1.0 [2.36, d, *J* 1.0] (3 H); 2.85, t (2 H); 6.63br, s [6.99, d, *J* 1.0] (1 H); 7.35—7.55, m (3 H); 7.80—8.0, m (2H)	187.5 (s) [—] [e]	113.9 (d) [116.6, d]	161.5 (s) [162.1, s]	33.7 (t), [32.7, t] 21.1 (t), [22.5, t]	22.1 (q), [24.6, q] 13.6 (q), [13.6, q]
(1c)	A	67/33	2.50, d, *J* 1.0 [2.38, d, *J* 1.0] (3 H); 4.11, s [4.13, s] (2 H); 6.64br, s [6.98, q, *J* 1.0] (1 H); 7.2—7.5, m (8 H), 7.65, m (2 H)	187.7 (s) [—] [e]	114.5 (d) [116.8, d]	161.7 (s) [160.2, s]	36.9 (t), [35.9, t]	21.6 (q), [24.8, q]
(1d)	A	54/46	2.51, d, *J* 1.1 [1.98, d, *J* 1.1] (3 H); 6.39, q, *J* 1.1 [7.07, q, *J* 1.1] (1 H); 7.3—7.7, m (8 H); 7.9—8.05, m (2 H)	188.5 (s) [187.9, s]	115.5 (d) [161.2, d]	161.7 (s) [161.9, s]	25.8 (q) [21.1, q]	
(1e)	A	0/100 [f]	1.09, t (3 H); 2.38, q (2 H); 7.06, s (1 H); 7.4—7.55, m (8 H); 7.9—8.0, m (2 H)	188.3 (s)	119.6 (d)	163.6 (s)	27.1 (t),	14.3 (q)
(1f)	B	67/33	1.39, t [1.37, t] (3 H); 2.92, q [2.80, q] (2 H); 6.90, d, *J* 14.9 [7.07], d, *J* 9.8] (1 H); 7.35—7.6, m (3 H); 7.85—8.05, m (3 H)	186.9 (s) [—] [e]	118.9 (d) [116.2, d]	148.9 (d) [152.5, d]	26.6 (t), [30.7, t]	14.0 (q), [14.4, q]
(1g)	B	55/45	6.84, d, *J* 14.9 [7.13, d, *J* 9.8] (1 H); 7.3—7.6, m (8 H); 7.9—8.05, m (2 H); 8.06, d, *J* 14.9 [—] [h]	188.9 (s) [187.2, 2]	116.3 (d) [119.8, d]	152.0 (d) [148.7, d]		
(1h)	A	100/0 [g]	0.96, t (3 H); 1.25—1.8, m (4 H); 2.17, s, (3 H); 2.37, d, *J* 1.0 (3 H); 2.78, t (2 H); 5.92br, s (1 H)	194.5 (s)	116.3 (s)	159.3 (s)	31.5 (q), 29.5 (t), 21.5 (q),	31.2 (t), 22.1 (t), 13.6 (q)
(1i)	A	88/12	1.99, s [2.21, s] (3 H); 2.40, d, *J* 1.0, [1.81, d, *J* 0.7] (3 H); 5.67br, s [6.32br, s] (1 H); 7.3—7.65, m (5 H)	194.9 (s) [—] [e]	118.3 (d) [119.8, d]	159.5 (s) [158.1, s]	31.5 (q) [30.3, q]	20.6 (q), [24.9, q]
(1j)	B	28/72	1.05, t [1.33, t] (3 H); 2.26, s [1.78, s] (3 H); 2.38, q [2.80, q] (2 H); 6.23, s [6.07, s] (1 H); 7.25—7.5, m (5 H)	195.8 (s) [—] [e]	123.3 (d) [121.7, d]	160.3 (s) [158.5, s]	30.6 (q), [26.9, q] 14.2 (q) [12.9, q]	26.9(t) [30.7, t]
(1k)	B	0/100 [i]	2.34, s (3 H; 6.48, s (1 H); 7.0—7.6, m (10 H)	196.1 (s)	123.4 (d)	159.0 (s)	30.7 (q)	
(1l)	A	100/0	1.34, t (3 H); 1.95—2.1, m (2 H); 2.1—2.55, m (4 H); 2.84, q (2 H), 5.85br, s (1 H)	195.4 (s)	119.3 (d)	165.4 (s)	37.4 (t), 25.3 (t), 13.0 (q)	30.9 (t), 23.0 (t),

[a] The *E*/*Z* ratios were determined by integration of the ^1H n.m.r. spectra. The *E*- and *Z*-isomers of (1) were assigned structures from the similarity in their α-proton resonances compared with the α-proton resonances in the pure *E*- or *Z*-isomers of (1a) and (1b) which were separated by silica-gel column chromatography (ref. 9). [b] Data for the minor isomer, where different from data for the major isomer, are given in square brackets. *J* Values are in Hz, and total proton intensities (major + minor isomer) are given in parentheses. [c] Aromatic carbon resonances are omitted. [d] Data for the minor isomer are in square brackets. [e] Not observed. [f] (1e) was shown to be the *Z*-isomer by the similarity of its u.v. spectrum [$\lambda_{max.}$ (EtOH) (ε) 252 (1.2×10^4) and 333 nm (1.81×10^4) to that of the *Z*-isomer of (1a) (see ref. 9). [g] $\lambda_{max.}$ (EtOH) (ε) 244 (3.1×10^3) and 290 nm (1.80×10^4). [h] The β-olefinic proton resonance was contained in the 7.9—8.05 resonance. [i] $\lambda_{max.}$ (EtOH) (ε) 259 (7.2×10^3) and 308 nm (1.00×10^4).

of (1a) with $NaBH_4$ in the presence of cobalt(III) chloride ($CoCl_2$) or nickel chloride ($NiCl_2$) gave the saturated ketone butyrophenone (5a). However, $NaBH_4$–$FeCl_2$, $NaBH_4$–$FeCl_3$, $NaBH_4$–CuI, $NaBH_4$–$CuCl_2$, and $LiAlH_4$–$CoCl_2$ showed no activity at all for the reduction of (1a). The ketones (1b, d—f, and j) were also reduced with $NaBH_4$ in the presence of $CoCl_2$ to give the saturated ketones (5a, e, f, and j). In order to compare the catalytic properties of the metal halides, reactions were studied with 1.0 : 2.0 : 0.1 ratios of (1) : $NaBH_4$: metal halide. The results (Table 4) show that the ketones (1a, b, d—f, and j) are reduced to the saturated ketones (5a, e, f, and j) by the combination of $NaBH_4$ with a catalytic amount of $CoCl_2$ or $NiCl_2$.

TABLE 2

Yields of reduction products (2) and (3)

Reducing reagent [b]	Solvent	% Yield [a] (2)	(3)	Other	(1) recovered
(1a) $LiAlH_4$	Et_2O	94.5			1.0
(1a) $NaBH_4$	EtOH	50.5			23.0
(1b) $LiAlH_4$	Et_2O	78.5			Trace
(1c) $LiAlH_4$	Et_2O	73.0		$PhCH_2SH$ (49)	Trace
(1c) $NaBH_4$	MeOH	42.5		$PhCH_2SH$ (32)	40.5
(1d) $LiAlH_4$	Et_2O	51.5		PhSH (51)	8.5
(1d) $NaBH_4$	EtOH	69.0		PhSH (21)	10.0
(1e) $LiAlH_4$	Et_2O	Trace	91.5		Trace
(1e) $NaBH_4$	EtOH	37.5	14.5		36.0
(1f) $LiAlH_4$	Et_2O	71.0			Trace
(1g) $LiAlH_4$	Et_2O	4.0	85.5	PhSH (7.5)	Trace
(1g) $NaBH_4$	MeOH	49.0		PhSH (30.5)	20.0
(1h) $LiAlH_4$	Et_2O	27.5			Trace
(1h) $NaBH_4$	MeOH	14.5			10.0
(1i) $LiAlH_4$	Et_2O	62.5		PhSH (6.5)	7.0
(1i) $NaBH_4$	MeOH	22.0		PhSH (6.0)	5.5
(1j) $LiAlH_4$	Et_2O		100		Trace
(1j) $NaBH_4$ [c]	MeOH	18.5			69.5
(1k) $LiAlH_4$	Et_2O		100		Trace
(1k) $NaBH_4$	MeOH	Trace			Trace
(1l) $LiAlH_4$	Et_2O	35.5			Trace
(1l) $NaBH_4$ [c]	MeOH	24.0			Trace

[a] The yields were determined by g.l.c. [b] 2 mol. equiv. unless otherwise noted. [c] 1 mol. equiv.

TABLE 3

Yields of (2) from the reduction of (1) with $NaBH_4$–$CeCl_3 \cdot 7H_2O$ in methanol

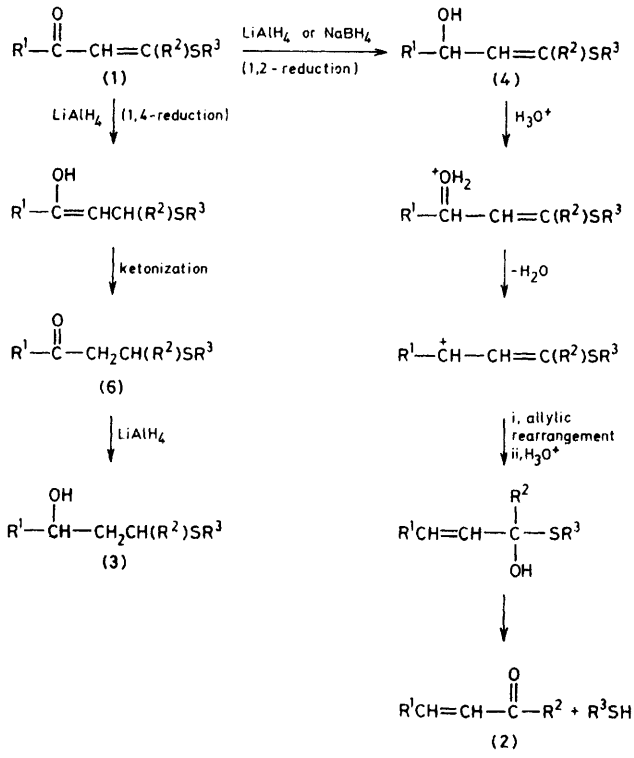
Mol. ratio (1) : $NaBH_4$: $CeCl_3$	% Yield [a] (2)	Other	(1) recovered
(1a) 1 : 2 : 1	78.0		4.0
(1d) 1 : 2 : 1	50.5	Ph_2S_2 (10) PhSH (5.5)	5.0
(1e) 1 : 2 : 1	54.0		20.0
(1f) 1 : 2 : 1	59.5		12.0

[a] The yields were determined by g.l.c.

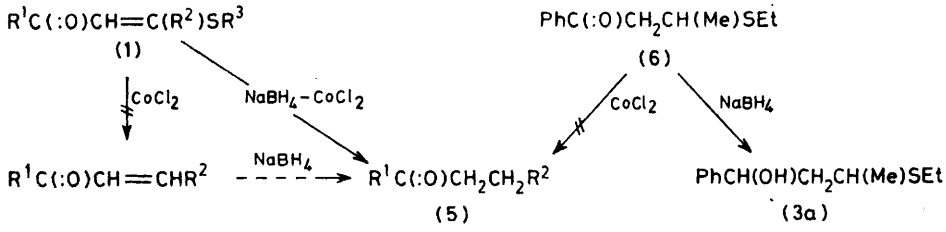
$$R^1C(:O)CH{=}C(R^2)SR^3 \xrightarrow[\text{in MeOH}]{NaBH_4\text{–metal halide}} R^1C(:O)CH_2CH_2R^2$$

(1a, b, d—f, and j) (5a, e, f, and j)

Treatment of (1a) with $CoCl_2$ in the absence of $NaBH_4$ resulted in complete recovery of (1a) and desulphenylation products were not observed. Furthermore, treatment of the γ-oxo-sulphide (6), which was prepared independently by the reaction of 1-phenylbut-2-en-1-one (3a) with ethanethiol in the presence of a catalytic amount of sodium methoxide, with $CoCl_2$ led to complete recovery of (6). The ketone (1a) and the sulphide (6) could not be desulphenylated under these conditions.



SCHEME 3



SCHEME 4

The sulphide (6) was also recovered quantitatively on treatment with $NaBH_4$–$CoCl_2$ under the same conditions as in the reduction of (1a). However, treatment of (6) with $NaBH_4$ gave the γ-hydroxy-sulphide (3a) quantitatively. From these results, the mechanism

for the formation of the saturated ketone (5) is not clear; it may proceed *via* selective 1,4-reduction and desulphenylation of (1) by the combination of $NaBH_4$ and metal halide (Scheme 4).

EXPERIMENTAL

All b.p.s and m.p.s are uncorrected. I.r. and n.m.r. spectra were recorded on Hitachi 260–30 and JEOL FX-100 spectrometers, respectively.

Preparation of β-Arylthio- or β-Alkylthio-αβ-Unsaturated Ketones (1).—*General procedure: method A*. A mixture of the diketone (3 g), the appropriate thiol (2 mol equiv.), and toluene-*p*-sulphonic acid (0.3 g) in benzene (50 ml) was refluxed for 15 h; the water produced was removed by a Dean–Stark separator during the reaction. The benzene solution was then washed with 10% aqueous sodium hydroxide and water, and dried ($MgSO_4$). After removal of the solvent, the residual oil was distilled to give the ketones (1a—e, h, i, and l). The pure *E*- and *Z*-isomers of (1a and b) could be separated by silica-gel column chromatography with benzene as eluant.[9] *Method B*. To a stirred mixture of the acetylenic ketone (1 g) and a catalytic amount of sodium methoxide in ether (30 ml) in an ice bath, a solution of the appropriate thiol (1.5 mol equiv.) in ether (20 ml) was added dropwise. The mixture was stirred for 5 h at 0 °C, poured into 10% aqueous sodium hydroxide, and extracted with ether. The extract was washed with water and dried ($MgSO_4$). After removal of the solvent, the residual oil was distilled to give the ketones (1f, g, j, and k). Yields and elemental analyses are in Table 5.

Reduction of (1) *with Lithium Aluminium Hydride* ($LiAlH_4$).—*General procedure*. To a stirred suspension of $LiAlH_4$ in dry ether (10 ml) was added dropwise a solution of (1) (1 mmol) in dry ether (10 ml) at room temperature. The mixture was stirred for an additional 2 h, refluxed for 30 min, poured into ice–water, and extracted with ether. The extract was washed with 10% hydrochloric acid, 10% sodium hydrogen carbonate, and water, and dried ($MgSO_4$). After removal of the solvent *in vacuo*, the residual oil was chromatographed on a silica-gel column with benzene as eluant to give the products (2) or (3), together with the starting material (1).

Ethyl 3-hydroxy-1,3-diphenylpropyl sulphide (3e) had b.p. 183 °C at 2 mmHg (kugelrohr temp.); $\nu_{max.}$ (film 3 400, 3 055, 3 030, 1 600, 1 495, 755, and 695 cm^{-1}; δ($CDCl_3$) 1.10 (t, 3 H), 2.21 (q, 2 H), 2.20 (m, 2 H), 3.87 (t, 1 H), 4.76 (m, 1 H), and 7.2br (s, 10 H) (Found: C, 75.2; H, 7.35. $C_{17}H_{20}OS$ requires C, 74.95; H, 7.4%).

3-Hydroxy-3-phenylpropyl phenyl sulphide (3g) had b.p. 145 °C at 2 mmHg (kugelrohr temp.); $\nu_{max.}$ (film) 3 400, 3 060, 3 040, 1 585, 1 490, 740, and 700 cm^{-1}; δ($CDCl_3$) 2.06 (m, 2 H), 2.95 (t, 2 H), 4.76 (t, 1 H), 7.2br (s, 10 H), and 8.15br (s, 1 H, exchangeable with D_2O) (Found: C, 73.55; H, 6.55. $C_{15}H_{16}OS$ requires C, 73.7; H, 6.6%).

Ethyl 3-hydroxy-1-phenylbutyl sulphide (3j) had b.p. 110 °C at 2 mmHg (kugelrohr temp.); $\nu_{max.}$ (film) 3 400, 3 060, 3 030, 1 600, 1 495, 765, and 705 cm^{-1}; δ($CDCl_3$) 1.12 (t, 3 H), 1.18 (d, 3 H), 1.91 (t, 2 H), 2.27 (q, 2 H), 3.8—4.2 (m, 2 H), and 7.24br (s, 5 H) (Found: C, 68.7; H, 8.55. $C_{12}H_{18}OS$ requires C, 68.5; H, 8.6%).

3-Hydroxy-1-phenylbutyl phenyl sulphide (3k) had b.p. 135 °C at 2 mmHg (kugelrohr temp.); $\nu_{max.}$ (film) 3 375, 3 060, 3 020, 1 585, 1 490, 1 480, 745, and 695 cm^{-1}; δ($CDCl_3$) 1.10 (d, 3 H), 1.95 (t, 2 H), 2.54br (s, 1 H), 3.93 (m, 1 H), 4.25 (t, 1 H), and 7.06br (s, 10 H) (Found: C, 74.1; H, 7.0. $C_{16}H_{18}OS$ requires C, 74.35; H, 7.0%).

Reduction of (1) *with Sodium Borohydride* ($NaBH_4$).—*General procedure*. To a stirred solution of $NaBH_4$ in

TABLE 4

Yields of the saturated ketones (5)

Run	Compound	Metal halide	Mol. ratio (1) : $NaBH_4$: metal halide	% Yield [a] (5)	Other products	Recovered (1)
1	(1a)	$CoCl_2$	1 : 2 : 0.1	71.0	PhCH(OH)CH_2CH(Me)SEt (3a) (15.5)	8.0
2	(1a)	$CoCl_2$	1 : 2 : 2	47.0	(3a) (trace)	44.0
3	(1a)	$NiCl_2$	1 : 2 : 0.1	68.5	(3a) (4.0)	23.5
4	(1a)	$NiCl_2$	1 : 2 : 2	50.0	(3a) (4.5)	44.0
5	(1b)	$CoCl_2$	1 : 2 : 2	57.0		30.0
6	(1d)	$CoCl_2$	1 : 2 : 0.1	44.0	PhSSPh (7) (34.5)	56.0
7	(1d)	$CoCl_2$	1 : 2 : 2	78.5	(7) (59.5)	21.0
8	(1e)	$CoCl_2$	1 : 2 : 0.1	84.5		10.0
9	(1e)	$CoCl_2$	1 : 2 : 2	75.0		15.5
10	(1f)	$CoCl_2$	1 : 2 : 0.1	70.5	PhCH(OH)CH_2CH_2SEt (3f) (15.0)	13.0
11	(1f)	$CoCl_2$	1 : 2 : 2	63.0	(3f) (32.0)	1.0
12	(1f)	$NiCl_2$	1 : 2 : 0.1	61.5	(3f) (24.0)	trace
13	(1j)	$CoCl_2$	1 : 2 : 0.1	73.0	MeCH=CHCOPh (3a) (2.5)	15.5
14	(1j)	$CoCl_2$	1 : 2 : 2	19.5	(2a) (21.0)	47.5

[a] The yields were determined by g.l.c.

TABLE 5

Yields and elemental analytical results for (1)

	B.p., *t*/°C [a] (*p*/mmHg) [m.p., *t*/°C]	% Yield	Elemental analyses [b]	% C	% H
(1c)	185 (2)	40	$C_{17}H_{16}OS$	76.1 (76.3)	6.0 (5.85)
(1d)	200 (2) [42.5—44]	61	$C_{16}H_{14}OS$	75.55 (75.75)	5.55 (5.45)
(1e)	[96—97]	57	$C_{17}H_{16}OS$	76.1 (75.75)	6.0 (5.95)
(1h)	80 (2)	59	$C_9H_{16}OS$	62.75 (62.4)	9.3 (9.2)
(1i)	110 (2)	54	$C_{11}H_{12}OS$	68.7 (68.4)	6.3 (6.2)
(1j)	115 (2)	82	$C_{12}H_{14}OS$	69.85 (69.65)	6.75 (6.75)
(1k)	[82.5—84]	75	$C_{16}H_{14}OS$	75.55 (75.7)	5.55 (5.55)
(1l)	150 (2)	66	$C_8H_{12}OS$	61.5 (61.85)	7.75 (7.8)

[a] Kugelrohr temperature. [b] Found figures in parentheses.

ethanol (10 ml) or methanol was added dropwise a solution of (1) (1 mmol) in ethanol (10 ml) at room temperature and the mixture was then stirred for an additional 2 h, poured into 10% hydrochloric acid, and extracted with dichloromethane. The extract was washed with 10% sodium hydrogen carbonate solution and water, and dried ($MgSO_4$). After removal of solvent, the residual oil was chromatographed on a silica-gel column with benzene as eluant to yield the αβ-unsaturated ketones (2).

Reduction of (1) *with* $NaBH_4$ *in the Presence of Metal Halides.—General procedure.* To a stirred solution of (1) (1 mmol) and the metal halide in methanol (10 ml) was added dropwise a solution of $NaBH_4$ in methanol (10 ml) at room temperature. The mixture was stirred for an additional 3 h, poured into 10% hydrochloric acid, and extracted with dichloromethane. The extract was washed with 10% aqueous hydrogen carbonate solution and water, and dried ($MgSO_4$). After removal of solvent, the residual oil was chromatographed on a silica-gel column with benzene as eluant to give the saturated ketones (5). Compounds (5a, f, j) were identified by direct comparison of their spectral data with those of authentic samples.

1,3-*Diphenylpropan*-1-*one* (5e) had m.p. 62—63 °C; $\nu_{max.}$ (KBr) 3 055, 3 025, 1 685, 1 600, 1 495, 750, and 695 cm^{-1}; δ($CDCl_3$) 2.85—3.5 (A_2B_2 m, 4 H), 7.0—7.6 (m, 8 H), and 7.8—8.1 (m, 2 H) (Found: C, 85.85; H, 6.65. $C_{15}H_{14}O$ requires C, 85.7; H, 6.7%).

Preparation of Ethyl 1-*Methyl*-3-*oxo*-3-*phenylpropyl Sulphide* (6a).—To a stirred solution of 1-phenylbut-2-en-1-one (1 g) and a catalytic amount of sodium methoxide in ether (15 ml) was added dropwise a solution of ethanethiol (1 g) in ether (15 ml) at 0 °C (ice bath). The mixture was stirred for 15 h at room temperature, poured into 10% aqueous sodium hydroxide, and extracted with ether. The extract was washed with 10% hydrochloric acid and water, and dried ($MgSO_4$). After removal of solvent, the residual oil was distilled to give the *sulphide* (6a) (72%); b.p. 123 °C at 2 mmHg (kugelrohr temp.); $\nu_{max.}$ (film) 3 060, 1 680, 750, and 695 cm^{-1}; δ($CDCl_3$) 1.26 (t, 3 H), 1.36 (d, 3 H, *J* 6.6 Hz), 2.60 (q, 2 H), 3.18 (m, 2 H), 3.35—3.55 (m, 1 H), 7.3—7.7 (m, 3 H), and 7.85—8.0 (m, 2 H) (Found: C, 69.25; H, 7.7. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.75%).

Reduction of (6a) *with* $NaBH_4$.—To a stirred solution of $NaBH_4$ (76 mg) in methanol (10 ml) was added dropwise a solution of (6) (1 mmol) in methanol (10 ml) at room temperature and the mixture was stirred for additional 5 h, poured into 10% hydrochloric acid, and extracted with dichloromethane. The extract was washed with 10% sodium hydrogen carbonate solution and water and dried ($MgSO_4$). After removal of the solvent, the residual oil was chromatographed on a silica-gel column with benzene as eluant to yield *ethyl* 3-*hydroxy*-1-*methyl*-3-*phenylpropyl sulphide* (3a) quantitatively, b.p. 110 °C at 2 mmHg (kugelrohr temp.); $\nu_{max.}$ (film) 3 400, 3 060, 3 030, 1 600, 1 495, 760, and 700 cm^{-1}; δ($CDCl_3$) 1.25 (t, 3 H), 1.33 (d d, 3 H, *J* 6.7 and 0.7 Hz), 1.6—2.2 (m, 2 H), 2.56 (q, 2 H), 2.5—3.1 (m, 1 H), 2.7br (s, 1 H, exchangeable with D_2O), 4.93 (m, 1 H), and 7.32br (s, 5 H) (Found: C, 68.55; H, 8.6. $C_{12}H_{18}OS$ requires C, 6.85; H, 8.6%).

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