Conversion of Tosylhydrazones of α-Halogeno-aldehydes and -ketones into the Corresponding Phenylthio- and Phenylseleno-derivatives

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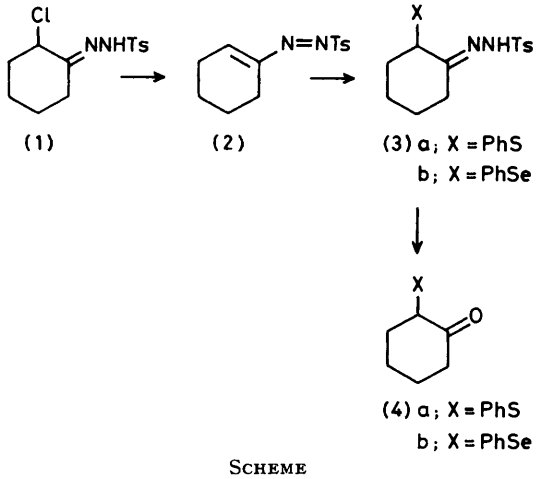
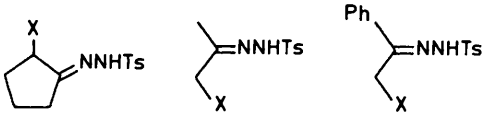
The tosylhydrazones of 2-chlorocyclohexanone, 2-chlorocyclopentanone, 1-chloropropanone, phenacyl chloride, 2-bromoheptanal and 2-bromo-2-methylpropanal (1), (5a), (6a), (7a), (8b), and (9b), respectively, reacted rapidly with thiophenol and an excess of triethylamine in tetrahydrofuran at −78 °C to give the corresponding α-phenylthio-substituted tosylhydrazones (3a), (5b), (6b), (7b), (8c), and (9c) in good yields. The α-phenylseleno-substituted tosylhydrazones (3b), (5c), (6c), (8d), and (9d) were similarly prepared, in satisfactory yields, by treating the corresponding α-halogeno-substituted tosylhydrazones with benzeneselenol and an excess of triethylamine. Several α-phenylthio-substituted carbonyl compounds and 2-phenylselenocyclohexanone (4b) were regenerated from the corresponding tosylhydrazones in good yields.

(TOLUENE-*p*-SULPHONYL)AZOALKENES (tosylazoalkenes),[1-7] such as 1-tosylazocyclohexene (2), are reactive intermediates which have much synthetic potential; they may readily be generated [3,6] from tosylhydrazones of α-halogeno-aldehydes and -ketones [*e.g.* 2-chlorocyclohexanone tosylhydrazone (1) (Scheme)] under mildly basic conditions. Tosylazoalkenes have a polarity opposite to that of enamines, enol ethers, enols, and related olefinic systems derived from aldehydes and ketones; thus they react with nucleophiles (*e.g.* enolate ions derived from 1,3-dicarbonyl compounds [5] and lithium diaryl-[7,8] and dialkyl-[7] cuprates) to give, following protonation, tosylhydrazones derived from α-substituted carbonyl compounds such as (3). Such reactions are of potential synthetic value, as the corresponding carbonyl compounds [*e.g.* (4)] may usually be regenerated from tosylhydrazones.[9] Furthermore, tosylhydrazones, and perhaps more particularly the corresponding mesitylene-2-sulphonyl- and 2,4,6-tri-isopropylbenzenesulphonylhydrazones,[10,11] are themselves valuable synthetic intermediates.



SCHEME

The original work on the preparation and reactions of simple tosylazoalkenes† was carried out by Caglioti and Rosini and their co-workers.[1-4] In an early paper, these workers reported [1] that 2-phenylthiocyclohexanone tosylhydrazone (3a) could be prepared from thiophenol and 1-tosylazocyclohexene (2). However, no experimental details were given. With the purpose of obtaining a clearer indication of the value of tosylazoalkenes in synthesis, we have investigated the reactions between these intermediates and various nucleophiles. We now report the results of such an investigation involving the conjugate bases of thiophenol and benzeneselenol.



(5) a; X = Cl
b; X = PhS
c; X = PhSe

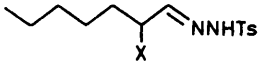
(6) a; X = Cl
b; X = PhS
c; X = PhSe

(7) a; X = Cl
b; X = PhS
c; X = PhSe

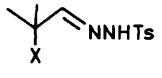
1-Tosylazocyclohexene [3] (2) was prepared by shaking an ethereal solution of 2-chlorocyclohexanone tosylhydrazone (1) with saturated aqueous sodium hydrogen carbonate, and was isolated in 76% yield. When it was treated, in a tetrahydrofuran solution under nitrogen at −78 °C, with a slight excess of thiophenol followed by a twofold excess of triethylamine, a rapid reaction ensued and 2-phenylthiocyclohexanone tosylhydrazone (3a) was isolated from the products as a crystalline solid in 78% yield (Table, experiment no. 1). A much higher overall yield of the tosylhydrazone (3a) was obtained from compound (1) when the isolation of the intermediate 1-tosylazocyclohexene (2) was omitted. Thus, when 2-chlorocyclohexanone tosylhydrazone (1) was treated with a slight excess of thiophenol and a twofold excess of triethylamine under the conditions described above, 2-phenylthiocyclohexanone tosylhydrazone (3a) was obtained in 80% isolated yield (Table, experiment no. 2). However, when 2-chlorocyclohexanone tosylhydrazone (1) was treated with *ca.* 1.1 molar equivalents of thiophenol and *ca.* 0.8 molar equivalents of triethylamine under the same conditions, no phenylthiocyclohexanone

† Substituted tosylazoalkenes are involved as intermediates in the Eschenmoser fragmentation reaction (A. Eschenmoser, D. Felix, and G. Ohloff, *Helv. Chim. Acta*, 1967, **50**, 708; M. Tanabe, D. F. Crowe, and R. L. Dehn, *Tetrahedron Lett.*, 1967, 3943).

tosylhydrazone (3) could be detected in the products. It therefore follows that compound (1) is not converted into the phenylthio-derivative (3a) by direct displacement of chloride ion by thiophenolate ion, but that 1-tosylazocyclohexene (2) is an intermediate in this transformation. Apparently, unlike triethylamine (pK_a 10.87),[12] thiophenolate ion (pK_a 6.5) [12] is not a strong enough base to effect the elimination of the elements of hydrogen chloride from compound (1) and thereby convert it into the azo-intermediate (2). Thus, at least two molar equivalents of triethylamine are required if the transformation of (1) into (3a) is to go to completion. When the tosylhydrazones of 2-chlorocyclopentanone, 1-chloropropanone, and phenacyl chloride [(5a), (6a), and (7a), respectively] were each treated with a slight excess of thiophenol and a twofold excess of triethylamine under the conditions used in the conversion of (1) into (3a), the tosylhydrazones of 2-phenylthiocyclopentanone, 1-phenylthiopropanone, and 2-phenylthioacetophenone [(5b), (6b), and (7b)] were obtained (Table, experiments nos. 3, 4, and 5) in 82, 83, and 79% isolated yields, respectively.



(8) a; X = H
b; X = Br
c; X = PhS
d; X = PhSe



(9) a; X = H
b; X = Br
c; X = PhS
b; X = PhSe

The required intermediate 2-halogeno-derivatives of aldehyde tosylhydrazones were prepared by the bromination of the corresponding unsubstituted tosylhydrazones with phenyltrimethylammonium perbromide, according to the procedure of Rosini and Baccolini.[6] Crude 2-bromoheptanal tosylhydrazone (8b), obtained in this way from heptanal tosylhydrazone (8a), was treated with thiophenol and triethylamine under the conditions described above to give (Table, experiment no. 6) 2-phenylthioheptanal tosylhydrazone (8c) as a crystalline solid in 72% isolated yield. 2-Methylpropanal tosylhydrazone (9a) was similarly converted (experiment no. 7) into 2-methyl-2-phenylthiopropanal tosylhydrazone (9c). The latter compound was isolated as a crystalline solid in 75% overall yield.

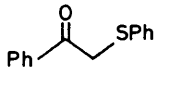
Tosylhydrazones of α-halogeno-ketones and -aldehydes were also found to react rapidly with benzeneselenol and triethylamine, in tetrahydrofuran at −78 °C, to give the corresponding phenylseleno-derivatives in satisfactory yields. In this way, the tosylhydrazones of 2-phenylselenocyclohexanone, 2-phenylselenocyclopentanone, and 1-phenylselenopropanone [(3b), (5c), and (6c), respectively] were prepared (Table, experiments nos. 8, 9, and 10) from (1), (5a), and (6a), and were isolated as crystalline solids in yields of 68, 64, and 72%, respectively. The tosylhydrazones of 2-phenylselenoheptanal and 2-methyl-2-phenylselenopropanal [(8d) and (9d), respectively] were, like the corresponding phenylthio-derivatives (8c) and (9c), prepared from the unsubstituted tosylhydrazones (8a) and (9a) *via* the intermediate 2-bromo-derivatives (8b) and (9b); they were isolated (experiments nos. 11 and 12) as crystalline solids in 69 and 67% overall yields, respectively.

TABLE

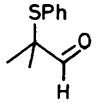
Preparation of α-phenylthio- and α-phenylseleno-substituted tosylhydrazones

Expt. no.	Substrate	Nucleophile	Product [b]	Isolated yield (%)	M.p. (°C)
1	(2)	PhS^-	(3a)	78	139.5—140
2	(1)	PhS^-	(3a)	80	
3	(5a)	PhS^-	(5b)	82	141
4	(6a)	PhS^-	(6b)	83	126.5—127.5
5	(7a)	PhS^-	(7b)	79	93—94
6	(8b) [a]	PhS^-	(8c)	72 [c]	110.5—111.5
7	(9b) [a]	PhS^-	(9c)	75 [c]	129—130
8	(1)	$PhSe^-$	(3b)	68	124.5—125
9	(5a)	$PhSe^-$	(5c)	64	134—135.5
10	(6a)	$PhSe^-$	(6c)	72	121—122
11	(8b) [a]	$PhSe^-$	(8d)	69 [c]	92.5—93
12	(9b) [a]	$PhSe^-$	(9d)	67 [c]	98—100 (decomp.)

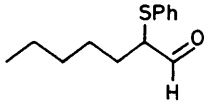
[a] 2-Bromoheptanal tosylhydrazone (8b) and 2-bromo-2-methylpropanal tosylhydrazone (9b) were obtained by brominating (8a) and (9a), respectively, with phenyltrimethylammonium perbromide. The crude bromo-compounds were used without further purification. [b] The ^1H n.m.r. spectra of these products suggested that all except (6b) and (7b) were pure geometrical isomers. The latter two products appeared to be mixtures of geometrical isomers in the ratios of *ca.* 4 : 1 and 2 : 1, respectively. [c] These are overall yields based on heptanal tosylhydrazone (8a) and 2-methylpropanal tosylhydrazone (9a) as starting materials.



(10)



(11)



(12)

We finally carried out a preliminary investigation into the possibility (see above) of preparing α-phenylthio- and α-phenylseleno-aldehydes and -ketones from their tosylhydrazones. A number of carbonyl regeneration procedures have been reported [9] and it seemed likely that treatment with boron trifluoride–diethyl ether in aqueous acetone [13] would be an effective procedure for the particular tosylhydrazones concerned. Treatment of 2-phenylthiocyclohexanone tosylhydrazone (3a) with an

excess of boron trifluoride–diethyl ether in acetone–water (10 : 1 v/v) for 16 h at room temperature gave, after work-up, 2-phenylthiocyclohexanone (4a) as a crystalline solid in 89% isolated yield. This procedure was also used for the preparation of 2-phenylthioacetophenone (10) and 2-methyl-2-phenylthiopropanal (11) from their tosylhydrazones (7b) and (9c), and the carbonyl compounds (10) and (11) were isolated in yields of 77 and 93%, respectively. The conversion of 2-phenylthioheptanal tosylhydrazone (8c) into the corresponding aldehyde (12) proceeded more slowly under the same reaction conditions; however, when paraformaldehyde [13] was added to the reaction mixture, 2-phenylthioheptanal (12) was obtained in good yield after 16 h. Finally, 2-phenylselenocyclohexanone (4b) was prepared from its tosylhydrazone (3b) under the conditions used (see above) for the conversion of (3a) into 2-phenylthiocyclohexanone, and was isolated as a crystalline solid in 87% yield.

It seems reasonable to conclude from the present study that the reactions between α-halogeno-derivatives of tosylhydrazones and the conjugate bases of thiophenol and benzeneselenol constitute general procedures for the preparation of α-phenylthio- and α-phenylseleno-substituted tosylhydrazones. These reactions, which may be assumed to proceed *via* tosylazoalkene intermediates, occur readily under very mild conditions and lead to substituted tosylhydrazones in satisfactory to good yields (Table). Although, in the present study, no α-phenylthio- or α-phenylseleno-substituted mesitylene-2-sulphonyl- or 2,4,6-tri-isopropylbenzenesulphonyl-hydrazones have been prepared, the mildness of the reaction conditions make it very likely that more hindered and potentially more synthetically useful [10,11] substituted arenesulphonylhydrazones such as these could be prepared in the same way.

While α-phenylthio [14,15] (and α-methylthio [15,16]) derivatives of tosylhydrazones have been used as intermediates in 1,2-carbonyl transposition reactions, another obvious application of the present work is in the preparation of α-arylthio- and α-arylseleno-derivatives of aldehydes and ketones which, as indicated above, may readily be obtained from the corresponding tosylhydrazones. Both α-sulphenylated [17] and α-selenenylated [18] carbonyl compounds are of considerable value as synthetic intermediates. Both series of compounds are usually prepared [17b,18] by reactions between enolate ions or protected enols derived from aldehydes and ketones and *electrophilic* sulphenylating or selenenylating agents. The reaction between an α-halogeno-carbonyl compound and the conjugate base of a thiol or a selenol (*i.e.* a *nucleophilic* sulphenylating or selenenylating agent) can lead [19,20] to what appear to be the products of reductive dehalogenation, in addition to the desired products of nucleophilic substitution. Such reductive dehalogenation has not been observed in the reactions between the latter nucleophiles and α-halogeno-derivatives of tosylhydrazones. Therefore, if it is desirable to use a *nucleophilic* sulphenylating or selenenylating agent in the preparation of an α-sulphenyl or an α-selenenyl derivative of an aldehyde or a ketone, the synthetic procedure described in this paper, involving an intermediate tosylhydrazone, may prove to be the method of choice.

EXPERIMENTAL

Unless otherwise stated, ^1H and ^{13}C n.m.r. spectra were measured with a Bruker HFX 90 FT spectrometer. Chemical shifts were measured in p.p.m. on the δ scale downfield from tetramethylsilane. Mass spectra were measured with AEI MS 30 and MS 902 spectrometers. U.v. spectra were measured with a Pye Unicam SP 8000 spectrometer. I.r. spectra were measured with Perkin-Elmer 257 and 297 spectrometers. T.l.c. was carried out on Merck silica gel 60 F_{254} plates.

Conversion of the Aldehydes and Ketones into their Toluene-p-sulphonylhydrazones (Tosylhydrazones).—The carbonyl compound (30 mmol) and tosylhydrazide (5.8 g, 31 mmol) were stirred together in methanol or diethyl ether (70 ml) at room temperature until t.l.c. [in dichloromethane–methanol (19 : 1 v/v)] indicated that the reaction was complete. After an appropriate quantity of water had been added to the products, the tosylhydrazone was allowed to crystallize in the refrigerator.

(*a*) 2-Chlorocyclohexanone was converted (30 min) into its tosylhydrazone (75%), m.p. 106—106.5 °C (lit.,[13] 113—114 °C).

(*b*) 2-Chlorocyclopentanone was converted (16 h) into *2-chlorocyclopentanone tosylhydrazone* (79%) (Found: C, 50.1; H, 5.2; N, 9.5. $C_{12}H_{15}ClN_2O_2S$ requires C, 50.3; H, 5.3; N, 9.8%), m.p. 120—121 °C, $\delta_H(CDCl_3)$ 1.8—2.6 (6 H, m), 2.43 (3 H, s), 4.67 (1 H, m), 7.31 (2 H, d, *J* 8.1 Hz), 7.85 (2 H, d, *J* 8.5 Hz), and 7.96 (1 H, br s).

(*c*) 1-Chloropropanone was converted (15 min) into *1-chloropropanone tosylhydrazone* (85%) (Found: C, 45.6; H, 5.0; N, 10.7. $C_{10}H_{13}ClN_2O_2S$ requires C, 46.1; H, 5.0; N, 10.7%), m.p. 108—109 °C; δ_H ($CDCl_3$) 1.91 (3 H, s), 2.43 (3 H, s), 4.04 (2 H, s), 7.32 (2 H, d, *J* 8.5 Hz), 7.84 (2 H, d, *J* 8.5 Hz), and 8.19 (1 H, br s).

(*d*) Phenacyl chloride was converted (8 h) into *2-chloroacetophenone tosylhydrazone* (82%) (Found: C, 55.2; H, 4.6; N, 8.6. $C_{15}H_{15}ClN_2O_2S$ requires C, 55.8; H, 4.7; N, 8.7%), m.p. 126—137 °C, δ_H ($CDCl_3$) includes the following signals: 2.41 (*ca.* 1.3 H, s), 2.45 (*ca.* 1.7 H, s), 4.32 (*ca.* 1.2 H, s), and 4.38 (*ca.* 0.8 H, s).

(*e*) 2-Methylpropanal was converted into *2-methylpropanal tosylhydrazone* (89%) (Found: C, 55.2; H, 6.9; N, 11.9. $C_{11}H_{16}N_2O_2S$ requires C, 55.0; H, 6.7; N, 11.7%), m.p. 100.5—101.5 °C, δ_H ($CDCl_3$) 1.00 (6 H, d, *J* 6.7 Hz), *ca.* 2.4 (1 H, m), 2.43 (3 H, s), 7.09 (1 H, d, *J* 5.3 Hz), 7.31 (2 H, d, *J* 7.6 Hz), and 7.81 (2 H, d, *J* 8.2 Hz).

(*f*) Heptanal was converted into its tosylhydrazone (74%), m.p. 66—67 °C.

1-Tosylazocyclohexene (2).—A solution of 2-chlorocyclohexanone tosylhydrazone (3.0 g, 10 mmol) in diethyl ether (500 ml) was shaken with saturated aqueous sodium hydrogen carbonate (100 ml) for 2—3 min. The organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated under reduced pressure (bath temperature < 20 °C). The residue was dissolved in hexane (150 ml) and the solution was cooled to −20 °C. The resulting yellow crystalline precipitate of 1-tosylazocyclohexene was filtered off (2.0 g, 76%), m.p. 60—61 °C (decomp.) [lit.,[3] 59—60 °C (decomp.)]

2-Phenylthiocyclohexanone Tosylhydrazone (3a).—(*a*) Thio-

phenol (0.56 ml, 0.605 g, 5.5 mmol) and then triethylamine (1.4 ml, 1.01 g, 10 mmol) were added to a cooled (acetone–solid CO_2 bath; −78 °C), stirred solution of 1-tosylazocyclohexene (1.32 g, 5.0 mmol) in tetrahydrofuran (50 ml) under nitrogen. As soon as the triethylamine had been added, the yellow colour disappeared. After a further period of 5 min, the products were poured into saturated aqueous sodium hydrogen carbonate (100 ml) and the mixture was extracted with dichloromethane (2 × 100 ml). The combined organic extracts were washed with aqueous sodium hydrogen carbonate, dilute hydrochloric acid, and water, and were then dried ($MgSO_4$). Evaporation of this solution gave a colourless solid. Crystallization of this material from ethyl acetate–hexane gave *2-phenylthiocyclohexanone tosylhydrazone* (Found: C, 60.7; H, 5.9; N, 7.5. Calc. for $C_{19}H_{22}N_2O_2S_2$: C, 60.9; H, 5.9; N, 7.5%) as colourless, fluffy crystals (1.46 g, 78%), m.p. 139.5—140 °C (lit.,[1] 164—165 °C), M^+, 374; δ_H ($CDCl_3$) 1.2—2.2 (6 H, m), 2.44 (5 H, m), 4.03 (1 H, m), 6.8—7.4 (7 H, m), and 7.55—7.9 (3 H, m).

(*b*) The above experiment was repeated using 2-chlorocyclohexanone tosylhydrazone (1.50 g, 5.0 mmol) instead of 1-tosylazocyclohexene. This was the only change made. The yield of crystallised 2-phenylthiocyclohexanone tosylhydrazone obtained was 1.50 g (80%).

(*c*) Thiophenol (0.56 ml, 0.605 g, 5.5 mmol) and then triethylamine (0.56 ml, 0.40 g, 4.0 mmol) were added to a cooled (acetone–solid CO_2 bath; −78 °C), stirred solution of 2-chlorocyclohexanone tosylhydrazone (1.50 g, 5.0 mmol) under nitrogen. After work-up under the conditions described above no 2-phenylthiocyclohexanone tosylhydrazone could be detected in the products.

2-Phenylthiocyclopentanone Tosylhydrazone (5b).—Thiophenol (0.56 ml, 0.605 g, 5.5 mmol) and then triethylamine (1.4 ml, 1.01 g, 10 mmol) were added to a cooled (−78 °C; acetone–solid CO_2), stirred solution of 2-chlorocyclopentanone tosylhydrazone (1.43 g, 5.0 mmol) in tetrahydrofuran (50 ml) under nitrogen. The products were worked up as in the above preparation of 2-phenylthiocyclohexanone tosylhydrazone and crystallized from ethyl acetate–hexane to give *2-phenylthiocyclopentanone tosylhydrazone* (1.38 g, 82%) (Found: C, 60.1; H, 5.6; N, 7.95. $C_{18}H_{20}N_2O_2S_2$ requires C, 60.0; H, 5.6; N, 7.8%), m.p. 141 °C, M^+, 360; δ_H ($CDCl_3$) 1.6—2.3 (6 H, m), 2.41 (3 H, s), 4.12 (1 H, m), 7.0—7.4 (7 H, m), 7.61 (1 H, s), and 7.76 (2 H, d, J 8.5 Hz).

1-Phenylthiopropanone Tosylhydrazone (6b).—Thiophenol (0.56 ml, 0.605 g, 5.5 mmol), triethylamine (1.4 ml, 1.01 g, 10 mmol) and 1-chloropropanone tosylhydrazone (1.30 g, 5.0 mmol) were allowed to react together as in the above preparation of 2-phenylthiocyclohexanone tosylhydrazone. Following the same work-up procedure, the products were isolated and crystallized from ethyl acetate–hexane to give *1-phenylthiopropanone tosylhydrazone* (1.38 g, 83%) (Found: C, 57.2; H, 5.4; N, 8.4. $C_{16}H_{18}N_2O_2S_2$ requires C, 57.5; H, 5.4; N, 8.4%), m.p. 126.5—127.5 °C, δ_H ($CDCl_3$) 1.72 (0.7 H, s), 1.86 (2.3 H, s), 2.45 (3 H, s), 3.50 (0.4 H, s), 3.64 (1.6 H, s), 6.9—7.4 (7 H, m), and 7.55—9.0 (3 H, m).

2-Phenylthioacetophenone Tosylhydrazone (7b).—Thiophenol (0.56 ml, 0.605 g, 5.5 mmol), triethylamine (1.4 ml, 1.01 g, 10 mmol) and 2-chloroacetophenone tosylhydrazone (1.61 g, 5.0 mmol) were allowed to react together as in the above preparation of 2-phenylthiocyclohexanone tosylhydrazone. Following the same work-up procedure, the products were isolated and crystallized from dichloromethane–hexane to give *2-phenylthioacetophenone tosylhydrazone* (1.56 g, 79%) (Found: C, 63.3; H, 5.1; N, 7.1. $C_{21}H_{20}N_2O_2S_2$ requires C, 63.6; H, 5.1; N, 7.1%), m.p. 93—94 °C, δ_H ($CDCl_3$) 2.45 (3 H, br s), 3.94 (1.3 H, s), 3.98 (0.7 H, s), 6.9—7.5 (13 H, m), 7.74 (1.25 H, d, J 8.2 Hz), and 7.90 (0.75 H, d, J 8.5 Hz).

2-Phenylthioheptanal Tosylhydrazone (8c).—Solid phenyltrimethylammonium perbromide (2.07 g, 5.5 mmol) was added over a period of 5 min to a stirred solution of heptanal tosylhydrazone (1.41 g, 5.0 mmol) in tetrahydrofuran at room temperature. After a further period of 10 min, the orange colouration of the reactants had faded and a solid had precipitated. Saturated aqueous sodium thiosulphate (2—3 drops) was added and the products were filtered. The residue was washed with tetrahydrofuran (20 ml) and the combined filtrate and washings were cooled to −78 °C (acetone–solid CO_2 bath) under nitrogen. Thiophenol (0.56 ml, 0.605 g, 5.5 mmol) and then triethylamine (1.4 ml, 1.01 g, 10 mmol) were added and the products were worked up as in the above preparation of 2-phenylthiocyclohexanone tosylhydrazone. Crystallization of the material obtained from ethyl acetate–hexane, gave *2-phenylthioheptanal tosylhydrazone* (1.40 g, 72%) (Found: C, 61.5; H, 6.7; N, 7.2. $C_{20}H_{26}N_2O_2S_2$ requires C, 61.5; H, 6.7; N, 7.2%), m.p. 110.5—111.5 °C, M^+, 390; δ_H ($CDCl_3$) 0.85 (3 H, m), 1.23 (6 H, m), 1.61 (2 H, m), 2.42 (3 H, s), 3.71 (1 H, quart., J 7.0 Hz), 7.0—7.4 (7 H, m), 7.69 (2 H, d, J 8.2 Hz), and 8.03 (1 H, s).

2-Methyl-2-phenylthiopropanal Tosylhydrazone (9c).—This compound was prepared from 2-methylpropanal tosylhydrazone (1.20 g, 5.0 mmol), phenyltrimethylammonium perbromide (2.07 g, 5.5 mmol), thiophenol (0.56 ml, 0.605 g, 5.5 mmol) and triethylamine (1.4 ml, 1.01 g, 10 mmol) by the procedure described above in the preparation of 2-phenylthioheptanal tosylhydrazone. Crystallization of the material obtained from ethanol–water gave *2-methyl-2-phenylthiopropanal tosylhydrazone* (1.30 g, 75%) (Found: C, 58.4; H, 5.6; N, 8.2. $C_{17}H_{20}N_2O_2S_2$ requires C, 58.6; H, 5.8; N, 8.0%), m.p. 129—130 °C, M^+, 348; δ_H ($CDCl_3$) 1.33 (6 H, s), 2.44 (3 H, s), 7.0—7.2 (8 H, m), 7.69 (2 H, d, J 8.5 Hz), and 7.76 (1 H, s).

2-Phenylselenocyclohexanone Tosylhydrazone (3b).—A solution of benzeneselenol (*ca.* 5.5 mmol), prepared [21] from diphenyl diselenide (0.86 g, 2.75 mmol) and 50% hypophosphorous acid (2.0 ml), in tetrahydrofuran (*ca.* 5 ml) was added to a cooled (acetone–dry ice bath; −78 °C), stirred solution of 2-chlorocyclohexanone tosylhydrazone (1.5 g, 5.0 mmol) in tetrahydrofuran (50 ml) under nitrogen. Triethylamine (1.4 ml, 1.01 g, 10.0 mmol) was then added and, after 5 min, the products were worked up as in the above preparation of 2-phenylthiocyclohexanone tosylhydrazone. Crystallization of the material obtained, from ethyl acetate–hexane, gave *2-phenylselenocyclohexanone tosylhydrazone* (1.43 g, 68%) (Found: C, 54.1; H, 5.1; N, 6.5. $C_{19}H_{22}N_2O_2SSe$ requires C, 54.15; H, 5.3; N, 6.65%), as colourless crystals, m.p. 124—125 °C, δ_H ($CDCl_3$) 1.3—2.2 (6 H, m), 2.4 (2 H, m), 2.43 (3 H, s), 4.13 (1 H, m), 6.9—7.45 (7 H, m), 7.61 (1 H, br s), and 7.79 (2 H, d, J 8.2 Hz).

2-Phenylselenocyclopentanone Tosylhydrazone (5c).—This compound was prepared in the same way as compound (3b), from 2-chlorocyclopentanone tosylhydrazone (0.572 g, 2.0 mmol), diphenyl diselenide (0.343 g, 1.1 mmol), 50% hypophosphorous acid (0.8 ml), and triethylamine (0.56 ml, 0.40 g, 4.0 mmol). Crystallization of the product obtained, from ethyl acetate—hexane, gave *2-phenylselenocyclopentanone tosylhydrazone* (0.518 g, 64%) (Found: C, 53.1; H, 5.0; N,

7.1. $C_{18}H_{20}N_2O_2SSe$ requires C, 53.1; H, 4.95; N, 6.9%), m.p. 134—135.5 °C, δ_H ($CDCl_3$) 1.6—2.4 (6 H, m), 2.42 (3 H, s), 4.30 (1 H, m), 7.0—7.65 (8 H, m), and 7.81 (2 H, d, *J* 8.5 Hz).

1-*Phenylselenopropanone Tosylhydrazone* (6c).—This compound was prepared in the same way as the tosylhydrazone (3b) from 1-chloropropanone tosylhydrazone (1.30 g, 5.0 mmol), diphenyl diselenide (0.86 g, 2.75 mmol), 50% hypophosphorous acid (2.0 ml), and triethylamine (1.4 ml, 1.01 g, 10.0 mmol). Crystallization of the product obtained from ethyl acetate–hexane gave 1-*phenylselenopropanone tosylhydrazone* (1.38 g, 72%) (Found: C, 50.4; H, 4.7; N, 7.5. $C_{16}H_{18}N_2O_2SSe$ requires C, 50.4; H, 4.8; N, 7.35%), m.p. 121—122 °C, M^+ 382, 380; δ_H ($CDCl_3$) 1.87 (3 H, s), 2.43 (3 H, s), 3.60 (2 H, s), 6.95—7.45 (7 H, m), 7.77 (2 H, d, *J* 8.5 Hz), and 7.95 (1 H, br s).

2-*Phenylselenoheptanal Tosylhydrazone* (8d).—2-Bromoheptanal tosylhydrazone was prepared as above from heptanal tosylhydrazone (1.41 g, 5.0 mmol) and phenyltrimethylammonium perbromide (2.07 g, 5.5 mmol). A tetrahydrofuran solution of benzeneselenol (*ca.* 5.5 mmol), prepared [21] from diphenyl diselenide (0.86 g, 2.75 mmol) and 50% hypophosphorous acid (2.0 ml), followed by triethylamine (1.4 ml, 1.01 g, 10.0 mmol), were added to a cooled (−78 °C), stirred solution of the crude 2-bromoheptanal tosylhydrazone in tetrahydrofuran (50 ml). After 5 min, the products were worked up as above and the material obtained was crystallized from ethyl acetate–hexane to give 2-*phenylselenoheptanal tosylhydrazone* (Found: C, 55.0; H, 5.9; N, 6.6. $C_{20}H_{26}N_2O_2SSe$ requires C, 54.9; H, 6.0; N, 6.4%) as colourless crystals (1.50 g, 69%), m.p. 92.5—93 °C, δ_H ($CDCl_3$) 0.85 (3 H, m), 1.22 (6 H, m), 1.66 (2 H, m), 2.43 (3 H, s), 3.77 (1 H, quart., *J* 7.3 Hz), 6.95—7.45 (8 H, m), 7.57 (1 H, br s), and 7.71 (d, *J* 8.5 Hz).

2-*Methyl*-2-*phenylselenopropanal Tosylhydrazone* (9d).—2-Bromo-2-methylpropanal tosylhydrazone was prepared as above from 2-methylpropanal tosylhydrazone (1.20 g, 5.0 mmol) and phenyltrimethylammonium perbromide (2.07 g, 5.5 mmol). The crude 2-bromo-2-methylpropanal was allowed to react with benzeneselenol (*ca.* 5.5 mmol; prepared as above) and triethylamine (1.4 ml, 1.01 g, 10.0 mmol) according to the procedure described above. Crystallization of the isolated product from ethyl acetate–hexane gave 2-*methyl*-2-*phenylselenopropanal tosylhydrazone* (Found: C, 51.5; H, 5.1; N, 7.0. $C_{17}H_{20}N_2O_2SSe$ requires C, 51.6; H, 5.1; N, 7.1%) as colourless crystals (1.33 g, 67%), m.p. 98—100 °C (decomp.), δ_H ($CDCl_3$) 1.44 (6 H, s), 2.44 (3 H, s), 6.95—7.45 (8 H, m), 7.71 (2 H, d, *J* 8.2 Hz), and 7.86 (1 H, br s).

2-*Phenylthiocyclohexanone* (4a).—2-Phenylthiocyclohexanone tosylhydrazone (0.748 g, 2.0 mmol), boron trifluoride–diethyl ether (0.4 ml, 3.25 mmol), acetone (20 ml) and water (2 ml) were stirred together at room temperature. After 16 h, the products were evaporated under reduced pressure and the residue was dissolved in diethyl ether. After the resulting solution had been extracted with 10% aqueous potassium hydroxide and water, it was dried ($MgSO_4$) and evaporated to give a colourless oily residue. Crystallization of this residue from ethanol gave 2-*phenylthiocyclohexanone* (Found: M^+, 206.0762. Calc. for $C_{12}H_{14}OS$: *M*, 206.0765) as colourless crystals (0.366 g, 89%), m.p. 57—58 °C (lit.,[22] 53—54 °C), $\nu_{max.}$ (CCl_4) 1 710s cm^{-1}; δ_H ($CDCl_3$) 1.4—2.5 (7 H, m), 2.7—3.1 (1 H, m), 3.83 (1 H, m), and 7.1—7.6 (5 H, m); δ_C ($CDCl_3$) 22.6, 27.3, 34.0, 39.1, 56.4, 127.3, 128.9, 131.8, 133.9, and 207.4.

2-*Phenylthioacetophenone* (10).—2-Phenylthioacetophenone was prepared from its tosylhydrazone (0.792 g, 2.0 mmol) by the acetone exchange procedure described above. Crystallization of the colourless oil obtained, from ethanol–water, gave 2-*phenylthioacetophenone* (Found: C, 73.3; H, 5.4; S, 13.7. $C_{14}H_{12}OS$ requires C, 73.65; H, 5.3; S, 14.0%) as colourless crystals (0.35 g, 77%), m.p. 51—52 °C (lit.,[23] 53—54 °C), M^+, 228; $\nu_{max.}$ (film) 1 675s cm^{-1}; δ_H ($CDCl_3$) 4.26 (2 H, s), 7.1—7.6 (8 H, m), and 7.92 (2 H, m); δ_C ($CDCl_3$) 41.1, 127.0, 128.7, 129.0, 130.4, 133.4, 134.8, 135.3, and 194.0.

2-*Methyl*-2-*phenylthiopropanal* (11).—2-Methyl-2-phenylthiopropanal was prepared from its tosylhydrazone (0.348 g, 1.0 mmol) by the above acetone exchange reaction, except that a reaction time of 4 d rather than 16 h was required. 2-*Methyl*-2-*phenylthiopropanal* (Found: M^+, 180.0611. $C_{10}H_{12}OS$ requires M^+, 180.0609) was obtained as a colourless oil (0.167 g, 93%); $\nu_{max.}$ (film) 1 710s cm^{-1}; δ_H ($CDCl_3$) 1.30 (6 H, s), 7.33 (5 H, m), and 9.33 (1 H, s); δ_C ($CDCl_3$) 21.2, 55.3, 128.9, 129.5, 129.9, 136.9, and 195.2.

2-*Phenylthioheptanal* (12).—2-Phenylthioheptanal tosylhydrazone (0.39 g, 1.0 mmol), boron trifluoride–diethyl ether (0.2 ml, 1.6 mmol), paraformaldehyde (0.30 g; equivalent to 10.0 mmol of formaldehyde), acetone (10 ml), and water (1 ml) were stirred together at room temperature. After 16 h, the products were worked up as above to give 2-*phenylthioheptanal* (Found: M^+, 222.1085. Calc. for $C_{13}H_{18}OS$: M^+, 222.1078) as an oil (0.195 g, 88%); $\nu_{max.}$ (film) 1 720s cm^{-1}; δ_H ($CDCl_3$) 0.89 (3 H, m), 1.15—2.0 (8 H, m), 3.51 (1 H, m), 7.33 (5 H, m), and 9.35 (1 H, d, *J* 4.1 Hz); δ_C ($CDCl_3$) 14.0, 22.4, 26.6, 27.8, 31.4, 56.8, 128.1, 129.1, 132.1, 132.8, and 195.1.

2-*Phenylselenocyclohexanone* (4b).—2-Phenylselenocyclohexanone was prepared from its tosylhydrazone (0.84 g, 2.0 mmol) by the acetone exchange reaction as described above. Crystallization of the isolated product from pentane gave 2-*phenylselenocyclohexanone* (Found: C, 56.8; H, 5.6. Calc. for $C_{12}H_{14}OSe$: C, 56.9; H, 5.6%) as colourless crystals (0.442 g, 87%), m.p. 54 °C (lit.,[24] 53—54 °C), M^+, 254 and 252; $\nu_{max.}$ (Nujol) 1 695s cm^{-1}; δ_H ($CDCl_3$) 1.4—2.0 (4 H, m), 2.0—2.45 (3 H, m), 2.75—3.2 (1 H, m), 3.91 (1 H, m), 7.0—7.3 (3 H, m), and 7.35—7.65 (2 H, m).

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