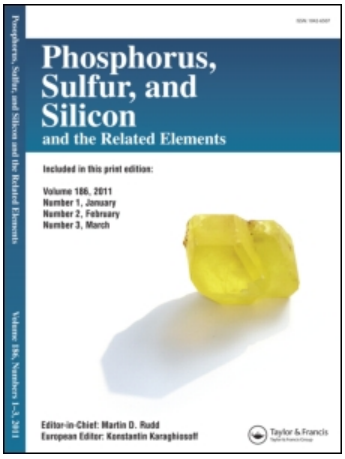

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PREPARATION AND REACTION OF N-TOSYL-AND N-ACYLSELENILIMINES

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PREPARATION AND REACTION OF N-TOSYL-AND N-ACYLSELENILIMINES

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N-Tosyl-Se,Se-diphenylselenilimines (Ia, hydrate state(Ib) of Ia), N-tosyl-Se-methyl-Se-phenylselenilimines (Ic), N-tosyl-Se,Se-dialkylselenilimines (Id–f), N-acyl-Se-aryl-Se-phenyl-selenilimines (IIa–e) and N-acyl-Se,Se-dibenzyl-selenilimine (IIf) were prepared. The pyrolyses of selenilimines (Ia,d,e, IIa-e) proceeded more readily than those of the corresponding sulfur derivatives. The pyrolyses of N-acyl-Se-aryl-Se-phenylselenylimines gave the corresponding isocyanates in good yields after treatment of the reaction mixture with aniline, together with aryl phenyl selenide. A kinetic study revealed that the rate of pyrolysis of N-benzoyl-Se,Se-diphenylselenilimine (IIa) was 300 times faster than that of the corresponding sulfilimine. The activation enthalpy and entropy were $\Delta H^{\ddagger} = 32.1$ kcal/mol and $\Delta S^{\ddagger} = 1.2$e.u. respectively for $Ph_2Se \rightarrow NCOPh$. Oxidations of N-tosyl- and N-benzoyl-Se,Se-diphenylselenilimine were carried out with hydrogen peroxide or potassium permanganate to obtain the corresponding selenoxides or selenones, respectively. Hydrolysis of N-tosyl- and N-benzoyl-Se,Se-diphenylselenilimines also took place more readily than that of the corresponding sulfilimines and the selenoxides and the amides were obtained in good yields at room temperature. When N-tosyl-Se,Se-pentamethyleneselenilimine (Ie) was treated with conc. sulfuric acid, a selenurane, Se-hydroxy-Se-(hydroxysulfoxy) selenane (III) was obtained in a high yield.

Recently, the first N-tosyl-selenilimines have been prepared[1–5] and found to be much more reactive than the corresponding sulfur analogous. Meanwhile, N-acyl-S,S-diphenylsulfilimines[6–8] were found to undergo both pyrolysis and photolysis, generating the corresponding isocyanate, the Curtius type rearrangement products. Because of the markedly higher reactivities of N-tosyl-selenilimines, the pyrolyses of N-acyl-selenilimines are expected to proceed more readily and the reaction may provide process for producing isocyanates. Thus, we have prepared various N-acyl-Se-aryl-Se-phenylselenilimines and studied a few typical reactions including the pyrolysis.

This paper describes the syntheses and interesting chemical behaviour of several selenilimines.

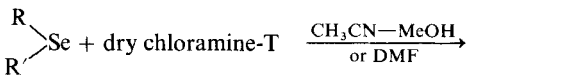
RESULTS AND DISCUSSION

Preparation of N-tosyl-Se,Se-diphenyl-, Se-alkyl-Se-phenyl- and Se-dialkylselenilimines Ia–f) Generally, N-tosyl-Se, Se-diphenyl (Ia, hydrate state (Ib) of Ia)-, Se-methyl-Se-phenyl (Ic)- and Se-Se-dialkylselenilimines (Id–f) were prepared by one of the following two methods.

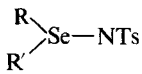
Method A: The selenide was treated with dehydrated sodium N-chloro-*p*-toluenesulfonamide (dry chloramine-T) in acetonitrile-methanol at room temperature or in N,N′-dimethylformamide(DMF) at 100°C.

Method B: Following the procedure previously reported,[5] a mixture of the selenoxide and *p*-toluenesulfonamide was refluxed in chloroform or acetonitrile. The N-tosyl-selenilimines thus obtained were characterized by spectroscopic and elemental analyses. The yields, mp and spectral data of a few selenilimines thus obtained are listed in Table I.

Method A



R,R′ = aryl, alkyl



(I)

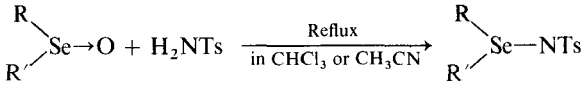
TABLE I

Yields and spectral data of  Se → NTs (I)

R′	Selenilimine R′	Method	Yield (%)	m.p. (°C)	IR(KBr, cm^{-1})	NMR(δ in $CDCl_3$)	Elemental analysis (%)	VU[MeOH, nm (log ε)]
Ia Ph	Ph	A	80.0	113.0–115.0 (lit[3] 105–6)	3055, 1590, 1570 1440, 1265, 1135 1085, 950, 570, 550	7.88–7.03 (m, 14H) 2.33 (s, 3H)	Found (Calcd for $C_{19}H_{17}NO_2SSe$) C 56.65 (56.71) H 4.00 (4.25) N 3.82 (3.48)	207 (4.54) 226 (4.42)
Ib Ph	Ph (hydrate)*	B	97.5	98.5–99.3 (lit[5] 98–99)	3325, 3040, 2925 1695, 1665, 1440 1332, 1150, 815 795, 555, 535	7.90–7.20 (m, 14H) 5.75 (br, s, 2H) 2.40 (s, 3H)	Found (Calcd for $C_{19}H_{19}NO_3SSe$) C 54.46 (54.29) H 4.52 (4.56) N 3.37 (3.33)	206 (4.45) 225 (4.42)
Ic Ph	CH_3	B	63.7	128.8–129.1 (lit[5] 129–130)	3048, 1597, 1445 1263, 1132, 1083 940, 890 575, 550	8.00–7.07 (m, 9H) 2.78 (s, 3H) 2.36 (s, 3H)	Found (Calcd for $C_{14}H_{15}NO_2SSe$) C 49.55 (49.41) H 4.38 (4.44) N 4.44 (4.11)	206 (4.18) 223 (4.24)
Id —$(CH_2)_4$-		A	81.5	125.5–126.8 (decomp) (lit[5] 125–127)	2930, 2860, 1590 1443, 1255, 1125 1080, 930 560, 545	7.67 (d, 2H) 7.13 (d, 2H) 3.58–1.93 (m, 8H) 2.36 (s, 3H)	Found (Calcd for $C_{11}H_{15}NO_2SSe$) C 43.39 (43.42) H 4.94 (4.96) N 4.25 (4.60)	226 (4.04)
Ie —$(CH_2)_5$-		A	98.5	129.8–130.8 (decomp)	3025, 2925, 1692 1442, 1263, 1128 1083, 939, 815 570, 550	7.73 (d, 2H) 7.18 (d, 2H) 3.09–2.80 (m, 4H) 2.35 (s, 3H) 1.89–1.45 (m, 6H)	Found (Calcd for $C_{12}H_{17}NO_2SSe$) C 45.61 (45.28) H 5.38 (5.38) N 4.37 (4.40)	205 (4.10) 226 (4.12)
If $PhCH_2$	H_2CPh	A	96.5	132.3–133.8 (lit[5] 118–120)	3050, 2905, 1590 1492, 1451, 1245 1119, 1083, 956 818, 765, 700 570, 550	7.57 (d, 2H) 7.28 (s, 10H) 7.03 (d, 2H) 4.21 (br, s, 4H) 2.33 (s, 3H)	Found (Calcd for $C_{21}H_{21}NO_2SSe$) C 58.57 (58.60) H 4.80 (4.91) N 3.45 (3.25)	206 (4.52) 226 (4.49)

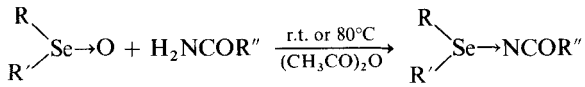
* The hydrate (Ib) was dried in vacuo at 105°C for 24h, giving anhydrate (Ia) in 91.6% yield.

Method B



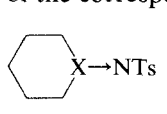
R.R′ = aryl, alkyl (I)

Preparation of N-acyl-Se-aryl-Se-phenylselenilimines (IIa–e) and Se,Se-dibenzylselenilimines (IIf) N-acyl-Se-aryl-Se-phenylselenilimines (IIa–e) and Se,Se-dibenzylselenilimines (IIf) were prepared similarly[9] by treating the corresponding selenoxides with acid amides in acetic anhydride at room temperature or 80°C. The yields and mp of N-acyl-Se-aryl-Se-phenylselenilimines thus prepared are summarized in Table II together with their spectral data.



R,R′ = aryl, benzyl (II)

The covalent radius of selenium (1.16 A) is longer than that of sulfur (1.02 A) and the electronegativity of selenium (2.4) is smaller than that of sulfur (2.5).[10] A length of Se—N bond in selenilimine is longer than that of the S—N bond in sulfilimine suggesting that N-tosyl- and N-acyl-selenilimines should have the ylide structure more distinctly than that of the corresponding sulfilimines. Indeed, the IR stretching frequency of the Se—N bond in selenilimine is shifted to a somewhat lower wave number than that of the S—N bond in sulfilimine. Accordingly, the Se—N bond should be more polarized than the S—N bond. Actually, as suggested by Klayman and Gunther,[10] all the N-tosyl-selenilimines have nearly identical absorption bands at around 550–590 cm^{-1} which can be assigned to the stretching frequencies of the Se—N bond similar to those of the S—N bond (960 cm^{-1}, S,S-diphenyl).[3,11] α-Protons of pentamethylene selenide moiety in N-tosyl-Se,Se-pentamethyleneselenilimine (Ie) appear at somewhat lower fields in the NMR spectrum than those of the corresponding sulfilimines.

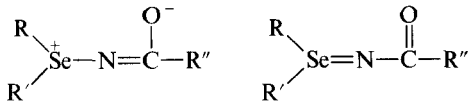


(Ie)

X=S 3.00–2.69 (*m*, 4H), 2.37 (*s*, 3H)

X=Se 3.09–2.80 (*m*, 4H), 2.35 (*s*, 3H)

N-Benzoyl-S,S-diphenylsulfilimine has strong characteristic IR absorption bands at around 1595, 1550(C=O) and 805 cm^{-1} (S—N),[11] those of the corresponding selenilimines appear at somewhat lower frequencies, i.e., 1585, 1535(C=O) and *ca.* 470(Se — N). NMR signals of N-benzoyl-Se,Se-diphenylselenilimine appear at δ8.25–8.03 ppm (m, 2H) and 7.90–7.16 (m, 13H), whereas the corresponding sulfilimine has signals at δ8.30–7.50 ppm (m, 15H). These spectral data are all in keeping with supposition that the N-acyl-selenilimine is best represented by the ylide structure rather than by the ylene structure, even in the case of the most stable N-tosyl-selenilimine.



Ylide type Ylene type

UV spectra of several N-tosyl- and N-acyl-selenilimines are shown in Tables I and II. A few N-tosyl-selenilimines (Ia, e) have their maximum absorption band only at around 223–226 nm with intensities (log ε_{max}) between 4.04–4.49, whereas N-acyl-selenilimine (IIa) has maximum absorption at 226 nm (log ε 4.41) and 259 nm (log ε 3.98). These UV absorption bands are similar to those of the corresponding sulfilimines.

Pyrolysis of N-Tosyl- and N-Acyl-selenilimines

Since the Se—N bonds in N-tosyl- and N-acyl-selenilimines are highly polarized and relatively weak, the pyrolysis is expected to proceed much more readily with the selenilimines than the corresponding sulfilimine. Indeed, upon heating in either tetralin or benzene the pyrolysis of N-tosyl-Se,Se-diphenyl- or Se,Se-dialkylselenilimine (Ia, d, e) and N-acyl-Se-aryl-Se-phenyl selenilimine (IIa–e) took place at lower temperature than that of the corresponding sulfilimines. After the pyrolysis, the products were separated by column chromatography packed with silica gel using chloroform as an eluent and identified by comparing their spectra with those of the authentic samples, as summarized in Tables III and IV. Probably, the source of hydrogen in these reactions should be considered as coming from the solvent. Thus, not only the pyrolysis of N-tosyl-Se,Se-diphenylselenilimine (Ia), but also that of N-tosyl-Se,Se-dialkylselenilimine (Id, e) proceeded more readily than the corresponding sulfur derivatives.[12] The pyrolysis of the N-acyl-Se-aryl-Se-phenylselenilimines (IIa–e) proceeded smoothly

TABLE II

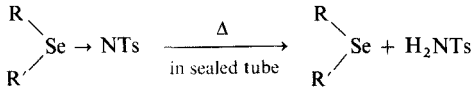
Yields and spectral data of $\begin{matrix} R \\ \diagdown \\ Se \\ \diagup \\ R' \end{matrix} \rightarrow NCOR''$ (II)

	R	Selenilimine R′	R″	Yield (%)	m.p. (°C)	IR(KBr, cm^{-1})	NMR(δ in $CDCl_3$)	Elemental analysis (%)	UV[MeOH, nm (log ε)]
IIa	Ph	Ph	Ph	98.0	124–6	3040, 1585, 1535	8.25–8.03 (m, 2H)	Found (Calcd for $C_{19}H_{15}NOSe$)	206 (4.61)
						1472, 1441, 1325	7.90–7.16 (m, 13H)	C H N	226 (4.41)
						1290, 870, 850		64.68 4.21 3.90	259 (3.98)
						750, 747, 712		(64.77) (4.29) (3.97)	
						675, 470			
IIb	Ph	Ph	p-ClC_6H_4	94.4	104–6	3035, 1582, 1538	8.10 (d, 2H)	Found (Calcd for $C_{19}H_{14}NOSeCl$)	234 (4.36)
						1478, 1440, 1330	7.83–7.18 (m, 12H)	C H N	262 (4.11)
						1315, 870, 850		59.05 3.62 3.82	
						742, 670		(59.00) (3.64) (3.62)	
IIc	Ph	Ph	CCl_3	96.2	118–20	3048, 1605, 1475	7.90–7.20 (m, 10H)	Found (Calcd for $C_{14}H_{10}NOSeCl_3$)	206 (4.59)
						1441, 1282, 1259		C H N	226 (4.31)
						821, 775, 740		42.90 2.61 3.33	260 (3.67)
						678		(42.72) (2.56) (3.55)	
IId	Ph	o-$CH_3OC_6H_4$	Ph	90.0	139–40	3045, 2930, 2830	8.30–6.70 (m, 14H)	Found (Calcd for $C_{20}H_{17}NO_2Se$)	207 (4.67)
						1585, 1475, 1325	3.80 (s, 3H)	C H N	226 (4.44)
						1295, 1241, 1020		63.04 4.42 3.87	264 (4.06)
						860, 755, 702		(62.83) (4.48) (3.66)	
IIe	Ph	o-$CH_3C_6H_4$	Ph	95.3	135–7	3040, 1583, 1525	8.28–7.18 (m, 14H)	Found (Calcd for $C_{20}H_{17}NOSe$)	206 (4.61)
						1320, 1290, 1018	2.58 (s, 3H)	C H N	227 (4.38)
						865, 750, 730		65.69 4.64 3.78	260 (3.99)
						700, 465		(65.57) (4.67) (3.82)	
IIf	$PhCH_2$	CH_2Ph	CCl_3	49.3	*	3060, 3030, 1610	7.30 (br, m, 10H)	—	—
						1590, 1580, 1495	4.28 (dd, 4H)		
						1285, 830, 810			
						760, 690, 670, 490			

* N-acyl-Se,Se-dibenzylselenilimine (IIf) is relatively more unstable compound.

TABLE III

Thermal decomposition product of I



	Selenilimine R	R′	Temp (°C)	Solvent	Product and yield (%) R—Se—R′	$TsNH_2$
Ia	Ph	Ph	240–50(1 h)	tetralin	70.2	68.4
Id	$-(CH_2)_4-$		130(1 h)	benzene	41.7	quant
Ie	$-(CH_2)_5-$		130(2 h)	benzene	37.5	87.5

at 160°C, whereas, the corresponding sulfur derivative was pyrolyzed at 200°C,[7] both affording the corresponding isocyanates in high yields, together with diphenyl selenide or diphenyl sulfide.

$$Ph_2S\rightarrow NCOR \xrightarrow{200^\circ C} Ph_2S + R-N=C=O$$

R = alkyl, aryl

$$Ph_2Se\rightarrow NCOR \xrightarrow{160^\circ C} Ph_2Se + R-N=C=O$$

R = aryl (RNHCONHPh)

A kinetic study of the pyrolysis of N-benzoyl-Se,Se-diphenylselenilimine (IIa) was carried out in DMF at around 140–160°C. The rate of the pyrolysis followed the first order kinetic equation. The rate constants or the effects of temperature on the rate of the pyrolysis of N-benzoyl-Se,Se-diphenylselenilimine and N-benzoyl-S,S-diphenylsulfilimines are summarized in Table V. The rate of pyrolysis of N-benzoyl-Se,Se-diphenylselenilimine (IIa) was found to be *ca.* 300 times than that of the corresponding sulfilimine. It is interesting to compare the activation parameters of both rearrangements. The activation enthalpy and entropy for $Ph_2Se \rightarrow NCOPh$ were $\Delta H^{\ddagger} = 32.1$ kcal/mol and $\Delta S^{\ddagger} = 1.2$ e.u. respectively.

Despite the large rate difference in the pyrolyses of the sulfilimine and selenilimine, the values of activation entropies are similar. Thus, the large rate difference is due solely to that of the enthalpy values. Since the Se—N bond in selenilimines is more polarized than the S—N semipolar bond in sulfilimines. Pyrolysis of the former takes place at a lower temperature than that of the sulfur derivative.

Oxidation of N-Tosyl- and N-Acyl-selenilimines

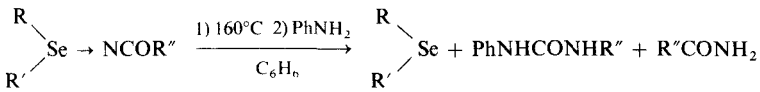
N-Tosyl-Se,Se-diphenylselenilimine (Ia) was oxidized with excess 30% hydrogen peroxide in acetic acid at room temperature. This gave the hydrate of N-tosyl-Se,Se-diphenylselenilimine (Ib) in 68.8% yield. When the N-benzoyl-Se,Se-diphenylselenilimine (IIa) was oxidized with excess 30% hydrogen peroxide in acetic acid at room temperature for 1 h, the corresponding diphenyl selenoxide and benzamide were obtained in 66.7% and 82.5% yields, respectively

$$Ph_2Se\rightarrow NTs \xrightarrow[\text{r.t. over night}]{30\%\ H_2O_2} Ph_2Se\rightarrow NHTs$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

(Ia) (Ib) 68.8%

TABLE IV

Thermal decomposition Product of II



	Selenilimine R	R′	R″	Product and yield (%) R—Se—R′	PhNHCONHR″	$R''CONH_2$
IIa	Ph	Ph	Ph	92.9	71.4	—
IIb	Ph	Ph	p-ClC_6H_4	82.6	55.4	—
IIc	Ph	Ph	CCl_3	93.2	—	76.9
IId	Ph	o-$CH_3OC_6H_4$	Ph	82.6	68.2	—
IIe	Ph	o-$CH_3C_6H_4$	Ph	92.7	70.7	—

TABLE V

Effect of temperature on pyrolysis of $Ph_2X \rightarrow NCOPh$ (X = S, Se) in DMF

	Temp. (°C)	k × s^{-1}	Rel. rate	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u)	γ
X = S	170.3	$1.68 \pm 0.09 \times 10^{-5}$				
	180.25	$4.52 \pm 0.14 \times 10^{-5}$				
	190.8	$1.22 \pm 0.07 \times 10^{-4}$				
	(130.0	$1.90 \pm 0.03 \times 10^{-7}$)	1	38.7 ± 0.1 (Ea = 39.5 ± 0.1 kcal/mol)	6.2 ± 0.3	0.999
X = Se	140.6	$1.64 \pm 0.3 \times 10^{-4}$				
	148.3	$3.81 \pm 0.2 \times 10^{-4}$				
	159.7	$9.72 \pm 0.4 \times 10^{-4}$				
	(130.0	$5.96 \pm 0.77 \times 10^{-5}$)	313.7	32.1 ± 2.3 (Ea = 32.9 ± 2.3 kcal/mol)	1.2 ± 5.3	0.998

$$Ph_2Se{\rightarrow}NCOPh \xrightarrow[\text{r.t. 1h}]{30\%\ H_2O_2} Ph_2Se{\rightarrow}O + H_2NCOPh$$
(IIa) 66.7% 82.5%

Rheinboldt, *et al.*[13] reported that treatment of diphenyl selenoxide with potassium permanganate at *ca.* 90°C afforded diphenyl selenone. Pasmurtseva, *et al.*[3] also reported that treatment of N-tosyl-Se,Se-diarylselenilimines with hydrogen peroxide or dinitrogen tetroxide afforded diaryl selenone. However, under our reaction conditions, the corresponding selenone of Ia was not obtained at all, the hydrate of Ia being only product formed in 68.8% yield.

In an attempt to prepare the selenoximine, N-tosyl- and N-benzoyl-Se,Se-diphenylselenilimines were oxidized in water by potassium permanganate at 120°C, following the usual procedure to prepare "solfoximine" from the N-tosyl-sulfilimine.[14] The N-tosyl-Se,Se- (Ia) and N-benzoyl-Se,Se-diphenylselenilimines (IIa) were oxidized with potassium permanagante in water at 120° for 10 min to give the corresponding diphenyl selenone, *p*-toluene-sulfonamide and benzamide in reasonable yields.

$$Ph_2Se{\rightarrow}NTs \xrightarrow[\text{in } H_2O]{KM\,O_4} Ph_2Se(=O)_2 + H_2NTs$$
(Ia) 54.0% 98.1%

$$Ph_2Se{\rightarrow}NCOPh \xrightarrow[\text{in } H_2O]{KMnO_4} Ph_2Se(=O)_2 + H_2NTs$$
(IIa) 49.1% 71.9%

Reduction of N-Tosyl-selenilimine by Triphenylphosphine

Treatment of N-tosyl-Se-methyl-Se-phenylselenilimine(Ic) with triphenylphosphine in chloroform at 80°C for 90 min, afforded methyl phenyl selenide and N-tosyl-triphenylphosphine imine in quantitative yields.

Furthermore, treatment of Ic with triphenylphosphine in acetic acid-benzene (1:1) at 80°C for 90 min also afforded methyl phenyl selenide and Ph_3PONH_2Ts in quantitative yields. Earlier we observed that treatment of N-tosyl-S-phenylsulfilimine with triphenylphosphine in water, alcohol,

TABLE VI

Reaction of N-tosyl-selenilimine with triphenylphosphine

	Reaction condition			Yields of product $PhSeCH_3$	$Ph_3P \rightarrow NTs$	Ph_3PONH_2Ts
Ph, CH_3 Se → NTs (Ic)	PPh_3	$CHCl_3$	60°C 1.5h	78.0	99.8	—
"	"	EtOH	80°C 1.0h	99.4	74.0	20.8
"	"	CH_3COOH $-C_6H_6$(1:1)	80°C 1.5h	92.0	—	94.0

acid or amine afforded the corresponding substituted sulfides, anhydrides, esters or amides.[15] However, similar treatment of the N-tosyl-selenilimine with triphenylphosphine, resulted only in the cleavage of the Se-N bond to give the corresponding selenide and the phosphine imine.

Hydrolysis of N-Tosyl- and N-Acyl-selenilimine

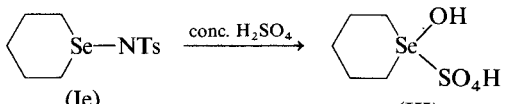
Cram and co-workers[16] reported that the hydrolysis of N-tosyl-S-methyl-S-*p*-tolylsulfilimine with sodium hydroxide in methanol afforded the corresponding sulfoxide in a high yield. Meanwhile, we reported[17] that alkaline hydrolyses of sulfilimines with hydroxide or methoxide anion in methanol or potassium *t*-butoxide in benzene afforded either the corresponding sulfoxide or the Pummerer type rearrangement products. N-Tosyl-S,S-diphenylsulfilimine, however, did not react even under refluxing with potassium hydroxide in methanol for 48 h. N-Tosyl-Se-Se-diphenylselenilimine and N-benzoyl-Se,Se-diphenylselenilimine are quite reactive and gave diphenyl selenoxide, *p*-toluenesulfonamide and benzamide in quantitative yields upon treatment with potassium hydroxide at room temperature as shown below. Thus, selenilimines are more susceptible to hydrolysis than the corresponding sulfilimines.

$$\underset{\text{(Ia)}}{Ph_2Se{\rightarrow}NTs} \xrightarrow[KOH-MeOH]{\text{r.t. 1h}} \underset{80.9\%}{Ph_2Se{\rightarrow}O} + \underset{89.5\%}{H_2NTs}$$

$$\underset{\text{(IIa)}}{Ph_2Se{\rightarrow}NCOPh} \xrightarrow[KOH-MeOH]{\text{r.t. 1h}} \underset{85.4\%}{Ph_2Se{\rightarrow}O} + \underset{87.9\%}{H_2NCOPh}$$

Reaction of N-Tosyl-Se,Se-pentamethyleneselenilimine (Ie) with conc. Sulfuric Acid

In an attempt to prepare N-unsubstituted selenilimine, N-tosyl-Se,Se-pentamethyleneselenilimine (Ie) was dissolved in conc. sulfuric acid at $-50°C$, then the solution was warmed at room temperature, as in the procedure to prepare "free sulfilimine" from N-tosyl-sulfilimine.[18] After 10 min, the color of the reaction mixture changed to yellow. When this yellow solution was poured into cold ether, colorless precipitates deposited. The crystalline precipitates were found to have the selenurane structure (III) by spectral and elemental analyses. Thus, the treatment with sulfuric acid resulted in the Se→N bond cleavage instead of N—SO_2 bond.



(Ie) (III)

Yield (%); 94.3%
mp(°C); 113–4

Drew[19] reported that when phenoxselenine dibromide was dissolved in a concentrated sulfuric acid, the color of the solution became yellow. The yellow color was thought to the formation of phenoxselenine sulfate which was, however, unable to be isolated by the previous workers. The product which we obtained appears to be the first example of the selenurane sulfate which is successfully isolated. In this reaction, sulfate anion apparently attacks the selenium atom of the selenilimine.

All these experimental results, together with the comparison of physical data with those of the corresponding sulfilimines clearly reveal that selenilimines are more reactive than the corresponding sulfilimines, since the Se—N bond is more polarized and hence weaker than the S—N bond.

EXPERIMENTAL

Preparation of N-Tosyl-selenilimine N-Tosyl-selenilimines were prepared according to known methods starting from selenides or selenoxides. Typical examples are shown below.

Method A Pentamethylene selenide[20] (300 mg, 2.0 mmol) was dissolved in 20 ml of acetonitrile-ethanol (4:1). To this was added 470 mg (2.1 mmol) of anhydrous chloroamine-T[21] at room temperature. After 30 min, solvent was removed in vacuo and the N-tosyl-Se,Se-pentamethyleneselenilimine (629.2 mg, 1.98 mmol) was obtained in 98.5% yield, mp 129.8–131.0°C. The N-tosyl-Se,Se-pentamethyleneselenilimine was recrystallized from chloroform-hexane.

Method B Diphenyl selenoxide[14] (250 mg, 1.0 mmol) was dissolved in acetonitrile (10 ml) containing anhydrous sodium sulfate. To this was added 171 mg (1.0 mmol) of p-toluenesulfonamide at room temperature. After refluxing the mixture for 2.5 h, the sodium sulfate was separated by filtration, the solvent was removed in vacuo and the residual solid was collected. N-Tosyl-Se,Se-diphenylselenilimine hydrate (409.5 mg, 0.98 mmol) was obtained in 98.0% yield, mp 98.5–99.5°C. The hydrate (300 mg, 0.71 mmol) was dried in vacuo at 105°C for 24 h, to give N-tosyl-Se,Se-diphenylselenilimine (262.1 mg, 0.65 mmol) in 91.6% yield. Other N-tosyl-selenilimines were prepared in a similar manner.

Their yields, spectral data and elemental analyses are given in Table I.

Preparation of N-Acyl-selenilimines N-Acyl-selenilimines were prepared according to Tarbell and Weaver's method[9] by condensation of selenoxides with acid amides. A typical example is shown below.

N-Benzoyl-Se,Se-diphenylselenilimine Diphenyl selenoxide (500 mg, 2.0 mmol) was dissolved in acetic anhydride (1–2 ml). To this was added 240 mg (2.0 mmol) of benzamide at 80°C. After 1 h, acetic anhydride was removed in vacuo and the residual solid was recrystallized from benzene. N-Benzoyl-Se,Se-diphenyl-selenilimine (690 mg, 1.96 mmol) was obtained in 98.0% yield, mp 124–6°C. Other N-acyl-Se-phenyl-Se-arylselenilimines were prepared similarly. Their yields, spectral data and elemental analyses are given in Table II.

Pyrolysis of N-Tosyl- or N-Acyl-selenilimine

Pyrolysis of N-tosyl-Se,Se-diphenylselenilimine (Ia), or N-tosyl-Se,Se-dialkylselenilimine (Id, e) was carried out by heating the compound in a sealed tube at 240–250°C or 130°C for 1–2h. After the usual work-up, the selenide was identified by GLC and p-toluenesulfonamide was obtained by decantation in reasonable yield (see Table III). Pyrolysis of N-acyl-Se-aryl-Se-phenylselenilimine (IIa) was carried out in benzene at 160°C for 1 h. A typical experiment is shown below.

Pyrolysis of N-Benzoyl-Se,Se-diphenylselenilimine (IIa) The selenilimine (100 mg, 0.28 mmol) in benzene (1 ml) was heated in a sealed tube at 160°C for 1 h. To this was added 50 mg of aniline at room temperature and the mixture was stirred for over night. After the usual work-up the selenide (61.1 mg, 0.26 mmol, 93%) was obtained by chromatography through silica gel eluted with benzene-hexane (1:1) and dipheny urea (43.3 mg, 0.20 mmol, 71.4%) was obtained by decantation (see Table IV).

Oxidation of N-Tosyl (Ia)- or N-Acyl-Se,Se-diphenyl-selenilimine (IIa)

N-Tosyl-Se,Se-diphenylselenilimine (200 mg, 0.48 mmol) was dissolved in 10 ml of acetic acid. To this was added excess 30% H_2O_2 at room temperature. After 12h the aqueous solution was extracted with chloroform. The chloroform solution was washed with water and dried over $MgSO_4$. The chloroform was then evaporated to yield Ib as white prisms (142.8 mg, 0.33 mmol, 68.8%). The structure was determined by IR spectral absorption as Ib.

N-Benzoyl-Se,Se-diphenylselenilimine (IIa) (200 mg, 0.57 mmol) was dissolved in acetic acid (10 ml). To this was added excess 30% H_2O_2 at room temperature. After 1 h, the aqueous solution was extracted with chloroform. The chloroform solution was dried over $MgSO_4$ and evaporated to yield white prisms. After the usual work-up, diphenyl selenoxide (94.3 mg, 0.38 mmol, 66.7%) and benzamide (56.8 mg, 0.47 mmol, 82.5%) were obtained by column chromatography through silica gel, eluted with ethyl acetate.

A solution of N-tosyl-Se,Se-diphenylselenilimine (Ia) (200 mg, 0.48 mmol) and potassium permanganate (76 mg, 0.48 mmol) in water (10 ml) was heated at 120°C for 10 min. The reaction mixture was extracted with ethyl acetate. The ethyl acetate solution was washed with water, dried over $MgSO_4$ and evaporated. After the usual work-up, diphenyl selenone (69.0 mg, 0.26 mmol, 54.0%) was obtained by column chromatography through silica gel, eluted with chloroform, whereas p-toluenesulfonamide (80.5 mg, 0.47 mmol, 98%) was obtained by column chromatography through silica gel, eluted with chloroform-methanol (19:1). The oxidation of N-benzoyl-Se,Se-diphenylselenilimine (IIa) was carried out similarly.

Reaction of N-Tosyl-Se-methyl-Se-phenylselenilimine with Triphenylphosphine

N-Tosyl-Se-methyl-Se-phenylselenilimine (Ic) (170 mg, 0.50 mmol) was dissolved in dry chloroform (1 ml) containing 140 mg (0.53 mmol) of triphenylphosphine. The mixture was heated in a sealed tube at 60°C for 1.5 h. After the solvent was evaporated, an oily residue was separated by adding hexane to the solution. Methyl phenyl selenide was obtained from the hexane layer and insoluble triphenyl N-tosyl-phosphine imine precipitated out in 78% (66 mg, 0.39 mmol), 99.8% (215 mg, 0.5 mmol) yields, respectively.

A mixture of Ic (170 mg, 0.5 mmol), triphenylphosphine (140 mg, 0.53 mmol) and benzene (0.5 ml) containing acetic acid (0.5 ml) was heated in a sealed tube at 80°C for 1.5 h. After the usual work-up, the products obtained were methyl phenyl selenide and Ph_3PONH_2Ts in 92% (78 mg, 0.46 mmol) and 94% (209 mg, 0.47 mmol) yields, respectively.

Hydrolysis of N-Tosyl- and N-Acyl-Se,Se-diphenyl-selenilimine

N-Tosyl-Se,Se-diphenylselenilimine (160 mg, 0.40 mmol) was treated with 70 mg (1.1 mmol) of potassium hydroxide in methanol (8 ml) at room temperature for 1 h. Diphenyl selenoxide was extracted with chloroform. The solution was then neutralized with 10% aqueous hydrochloric acid and p-toluenesulfonamide was extracted with chloroform. Diphenyl selenoxide and p-toluenesulfonamide were obtained in 80% (80.5 mg, 0.32 mmol) and 90% (61 mg, 0.36 mmol) yields, respectively.

N-Benzoyl-Se,Se-diphenylselenilimine (140 mg, 0.4 mmol) was allowed to react similarly. The products obtained were separated by chromatography through a silica gel packed column and identified by comparing their IR and NMR spectra with those of the authentic samples. Diphenyl selenoxide and benzamide were obtained in 85% (85 mg, 0.34 mmol) and 87.5% (42 mg, 0.35 mmol) yields, respectively.

Reaction of N-Tosyl-Se,Se-pentamethyleneselenilimine (Ie) with conc. sulfuric acid

N-Tosyl-Se,Se-pentamethyleneselenilimine (500 mg, 1.57 mmol) was dissolved in 2 ml conc. sulfuric acid at −50°C, and the mixture was heated at room temperature giving a yellow solution. After 10 min, the reaction mixture was added dropwise into cold ether at −50°C, colorless precipitates (400 mg, 1.52 mmol) were obtained in 96.8% yield. The precipitates were recrystallized from methanol-acetone. Se-Hydroxy-Se-(hydroxysulfonyloxy)-selenane 390 mg (1.48 mmol) was obtained in 94.3% yield, mp 113–4 C.

IR(KBr); 3400(br, OH), 2930, 1140(SO_4), 1120(SO_4H)
Mass(m/e); 150($M^+ - H_2SO_5$, 65.6%), 148(33.8%), 69($M^+ - H_2SeSO_5$, 86.9%), 68(37.5%), 67(36.3%), 64($M^+ - C_5H_{12}SeSO_3$, 74.4%), 41(100%)
Found; C, 23.26; H, 4.60% Calcd for $C_5H_{12}SeSO_5$; C, 22.82; H, 4.59%

Kinetics of N-benzoyl-Se,Se-diphenylselenilimine (IIa)

A typical kinetic procedure is as follows; to a 0.1 mol/l solution of N-benzoyl-Se,Se-diphenylselenilimine in DMF (10 ml) was added 170 mg of benzyl phenyl sulfide (0.085 mol/l) as an internal standard at room temperature. The solution (0.2 ml) was taken in a 1 ml ampoule by a 1 ml syringe. Several ampoules were then immersed in an oil-bath maintained at a desired temperature and the ampoules were taken out at various time intervals. The solution was quenched immediately with 0.5 ml of water in an ampoule. After addition of 0.2 ml of hexane, the solution was shaken vigorously for a while. The hexane layer was then separated and 2μl of the hexane solution was injected directly into a column of GLC. Gas chromatography was carried out under the following condition; column SE-30, 1 m × 2 mm, column temp. 140°C, He 0.7 kg/cm^2. The rate constants of the reaction were calculated by the first order kinetic equation, therefore a concentration change of diphenyl selenide is calculated from the relative peak-height of benzyl phenyl sulfide (internal standard) at each time. The activation parameters were calculated by the usual method. The data obtained are summarized in Table V.

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