Thermal Curtius Rearrangement of *N*-Acyl-*S,S*-diphenylsulfilimine

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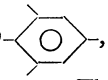
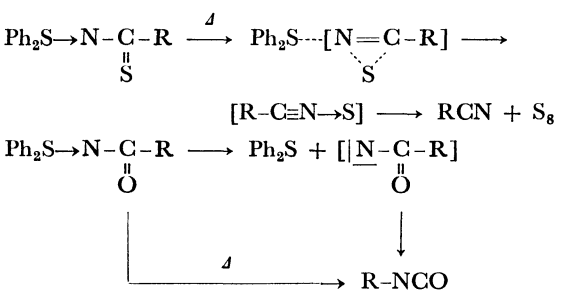
Several *N*-acyl-*S,S*-arylphenylsulfilimines were prepared and subjected to thermal decomposition. They decomposed readily at 130—190 °C to give isocyanates together with diphenyl sulfide, quantitatively. However, *N*-tosyl-*S,S*-diphenylsulfilimine did not decompose even upon heating at 200 °C for 24 h. A kinetic study revealed that the rates of pyrolysis of *N*-aroyl-*S,S*-arylphenylsulfilimines (*p*-Y-C_6H_4(Ph)S→$NCOC_6H_4$-X-*p*) are nicely correlated with the Hammett σ-values, $\rho_X=-1.2$ and $\rho_Y=+0.92$, respectively, being obtained. The activation enthalpies and entropies were $\Delta H^{\ddagger}=38.7$ kcal/mol and $\Delta S^{\ddagger}=6.0$ e.u. for Ph_2S→NCOPh and $\Delta H^{\ddagger}=32.3$ kcal/mol and $\Delta S^{\ddagger}=5.5$ e.u. for Ph_2S→NCO-  -, respectively. The rearrangement was accelerated considerably by *o*-methyl substituent in the aryl group. The effect of solvent on the rate of pyrolysis was small. The results indicate that the pyrolysis of sulfilimine proceeds *via* a concerted migration of the R group from carbonyl carbon to imino nitrogen similar to the Curtius type rearrangement of acid azide.

N-Tosylsulfilimines each having at least one β-hydrogen atom undergo facile intramolecular elimination (Ei) to afford olefin stereoselectively in high yields.[1] Meanwhile, *N*-tosylsulfilimines having no β-hydrogen atom, such as *N*-tosyl-*S,S*-dimethyl and *N*-tosyl-*S,S*-methylphenylsulfilimines are stable under the usual Ei conditions (benzene reflux) but decompose upon heating in DMSO or DMF at *ca.* 200 °C to afford interesting products as shown below.[2] In contrast, *N*-tosyl-*S,S*-diphenylsulfilimine is quite stable even upon heating at 200 °C and recovered almost quantitatively.[3]

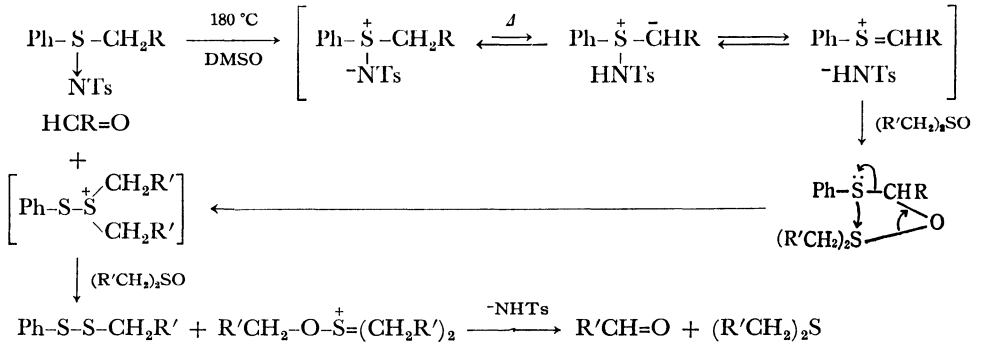
Yoshida *et al.*[4] found that *N*-thiocarbonyl-*S,S*-diphenylsulfilimines undergo pyrolysis at 70 °C to afford the corresponding nitriles, diphenyl sulfide and sulfur. They proposed that the pyrolysis proceeds *via* the initial migration of the thione sulfur to the imino nitrogen to form incipiently the nitrile sulfide which decomposes rapidly to afford the nitrile and sulfur. Thermally stable *N*-acyl-*S,S*-diphenylsulfilimines were found to undergo facile photolysis, resulting in the photochemical Curtius rearrangement *via* an incipient formation of the corresponding nitrene.[5] Synthetic utilization of the thermolysis of sulfilimines has recently been shown by Gilchrist *et al.*[6] and Tamura *et al.*[7]

In the course of a preliminary study on the sulfilimines, we found that *N*-benzoyl-*S,S*-diphenylsulfilimine decomposes quite readily when heated at 200 °C *in situ* and also in such solvents as DMF, tetralin and even EtOH in a sealed tube.[3] The products obtained in high yields by the pyrolysis were found to be diphenyl sulfide, phenyl isocyanate and *N,N'*-diphenylurea. The facile thermal decomposition of *N*-benzoyl-*S,S*-diphenylsulfilimine prompted us to investigate the thermolysis of various *N*-acyl-*S,S*-diarylsulfilimines, all of which have been found to afford the corresponding isocyanates and diaryl sulfides almost quantitatively. Thus, we carried out a kinetic study on the pyrolysis of *N*-acyl-*S,S*-diarylsulfilimines and found that these rearrangements proceed through the Curtius type rearrangement as in the ordinary thermal Curtius rearrangement in the thermolysis of *N*-acyl azides.

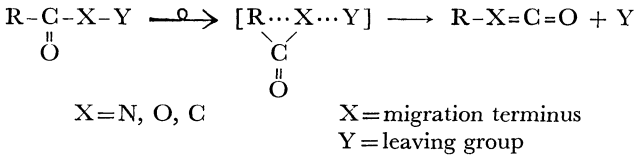


Scheme 2.

This paper describes detailed analysis of products, results of kinetic experiments on the Curtius type rearrangement of *N*-acyl-*S,S*-arylphenylsulfilimines and a plausible mechanism of the reaction in comparison with those of other reactions involving alkyl or aryl group migration from carbonyl group to electron deficient nitrogen or oxygen terminus.



Scheme 1.

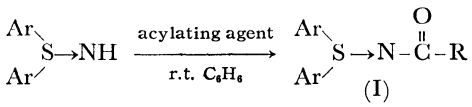


Scheme 3.

Results and Discussion

Preparation of N-*Acyl*-S,S-*diphenylsulfilimine.* *N*-Acyl-*S*,*S*-diphenylsulfilimines were prepared by acylating unsubstituted diphenylsulfilimine with appropriate acylating agents.[7] The yields and mp(°C) of sulfilimines thus prepared are summarized in Table 1 together with spectral data.

Pyrolyses of N-*Acyl*-S,S-*diphenylsulfilimines.* The pyrolysis of *N*-acyl-*S*,*S*-diphenylsulfilimines (Ia—f) was carried out by heating *in situ* or in such solvents as tetralin, DMF, toluene and EtOH. After the pyrolysis,

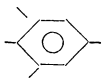


Scheme 4.

the products were separated by column chromatography or preparative GLC and identified by spectroscopic analysis by comparing their spectra with those of the authentic samples. The products thus obtained are summarized in Table 2. We see that the pyrolysis proceeds cleanly to afford the corresponding isocyanate (II) and diphenyl sulfide nearly quantitatively except in the case of the *N*-benzoyl (R=Ph) derivative which gives a small amount of the isocyanate and a substantial portion of the dimerized product which is similarly obtained by photolysis; thus the total yield of phenyl isocyanate incipiently formed by the thermolysis of Ia is also quantitative.

Kinetic Studies. A kinetic study of the pyrolysis of

Table 1. Yields and spectral data of Ar, Ar′S→NCOR (I)

	Sulfilimine (I) Ar	Ar′	R	Yield (%)	Mp (°C)	IR (cm^{-1})	NMR (δ, ppm, $CDCl_3$)	Elemental analysis (%)
a	Ph	Ph	-Ph	77.0	124—124.5	3050, 1595 1550, 1330 805	8.30—7.50 (m, 15H)	Found (Calcd for $C_{19}H_{15}NOS$) C H N 74.75 5.00 4.5 (74.7) (4.95) (4.6)
b	Ph	Ph	$-CH_2Ph$	59.8	120—121	3050, 1590 1570, 1445 1315, 1135	7.80—7.19 (m, 15H) 3.77 (s, 2H)	Found (Calcd for $C_{20}H_{17}NOS$) C H N 75.27 5.36 4.12 (75.21) (5.37) (4.39)
c	Ph	Ph	$-\underset{\text{Ph}}{\overset{\vert}{C}}HC_2H_5$	58.0	93.5—94.5	3050, 2950 1590, 1570 1475, 1440 1220	7.80—7.10 (m, 15H) 3.73 (t, 1H) 2.43—1.57 (m, 2H) 0.93 (t, 3H)	Found (Calcd for $C_{22}H_{21}NOS$) C H N 76.17 6.09 4.25 (76.04) (6.09) (4.03)
d	Ph	Ph		68.5	116—117	3050, 2900 1580, 1440 1275, 1250 1080	7.91—7.23 (m, 10H) 2.22—1.65 (m, 15H)	Found (Calcd for $C_{23}H_{25}NOS$) C H N 75.93 6.93 3.84 (75.99) (6.93) (3.85)
e	Ph	Ph		52.0	143—144	3050, 1610 1580, 1560 1480, 1445 1320, 1175 1100	7.92—7.67 (m, 4H) 7.57—7.33 (m, 6H) 6.77 (s, 2H) 2.33 (s, 6H) 2.22 (s, 3H)	Found (Calcd for $C_{22}H_{21}NOS$) C H N 76.00 5.00 3.99 (76.00) (6.09) (4.03)
f	Ph	Ph		62.9	96—97	3050, 1600 1580, 1560 1325, 1090	8.00—6.80 (m, 14H) 2.57 (s, 3H)	Found (Calcd for $C_{20}H_{17}NOS$) C H N 75.04 5.28 4.48 (75.20) (5.36) (4.38)
g	Ph	Ph	$-CH_3$[7]	95.0	87—88	3050, 1579 1560, 1475 1440, 1365 1310		Found (Calcd for $C_{14}H_{13}NOS$) C H N 69.1 5.40 5.70 (69.1) (5.40) (5.80)

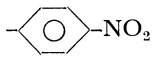
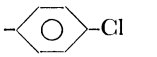
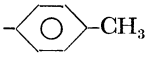
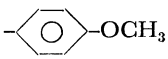
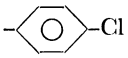
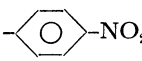
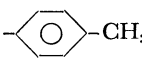
	Sulfilimine (I) Ar	Ar′	R	Yield (%)	Mp (°C)	IR (cm^{-1})	NMR (δ, ppm, $CDCl_3$)	Elemental analysis (%)
h	Ph	Ph	$-C_2H_5$	74.3	56—57	3040, 2960 1585, 1570 1360, 1235	7.72—7.17 (m, 10H) 2.50 (q, 2H) 1.22 (t, 3H)	Found (Calcd for $C_{15}H_{15}NOS$) C H N 69.83 5.80 5.56 (70.00) (5.87) (5.44)
i	Ph	Ph	$-CH(CH_3)_2$	81.5	60—61	3050, 2950 1580, 1570 1240	7.90—7.20 (m, 10H) 3.00—2.27 (m, 1H) 1.27 (d, 6H)	Found (Calcd for $C_{16}H_{17}NOS$) C H N 70.80 6.28 5.08 (70.81) (6.31) (5.16)
j	Ph	Ph	$-C(CH_3)_3$	70.5	64—65	3050, 2950 1580, 1560 1318, 1200	7.77—7.20 (m, 10H) 1.33 (s, 9H)	Found (Calcd for $C_{17}H_{19}NOS$) C H N 71.22 6.38 4.95 (71.54) (6.71) (4.90)
k	Ph	Ph		63.1	113—114	3050, 1560 1320	8.50—7.18 (m, 14H)	Found (Calcd for $C_{19}H_{14}N_2O_3S$) C H N 65.45 4.00 8.01 (65.12) (4.02) (7.99)
l	Ph	Ph		59.1	122—123	3040, 1585 1540, 1320 1300	8.07—7.13 (m, 14H)	Found (Calcd for $C_{19}H_{14}NOSCl$) C H N 67.15 4.04 4.12 (67.15) (4.15) (4.12)
m	Ph	Ph		70.7	154—155.5	3050, 1590 1550, 1320 900, 745	8.20—7.13 (m, 14H)	Found (Calcd for $C_{19}H_{14}NOSCl$) C H N 67.45 3.99 4.14 (67.15) (4.15) (4.12)
n	Ph	Ph		69.8	119—120	3050, 1590 1545, 1330	8.28—7.14 (m, 14H) 2.32 (s, 3H)	Found (Calcd for $C_{20}H_{17}NOS$) C H N 75.2 5.4 4.4 (74.6) (5.3) (4.3)
o	Ph	Ph		57.0	124.5—125.5	3050, 1600 1580, 1550 1320	8.23—6.73 (m, 14H) 3.77 (s, 3H)	Found (Calcd for $C_{20}H_{17}NO_2S$) C H N 71.89 5.13 4.24 (71.61) (5.10) (4.17)
p	Ph		Ph	83.2	84—85	3050, 1595 1555, 1480 1330, 1295	8.28—7.17 (m, 14H)	Found (Calcd for $C_{19}H_{14}NOSCl$) C H N 66.99 3.90 4.20 (67.15) (4.15) (4.12)
q	Ph		Ph	77.1	130—131	3050, 1595 1560, 1525 1350	8.30—7.13 (m, 14H)	Found (Calcd for $C_{19}H_{14}N_2O_3S$) C H N 65.40 3.90 7.96 (65.12) (4.02) (7.99)
r	Ph		Ph	76.3	125.5—126.5	3050, 1590 1550, 1325 1295	8.40—7.07 (m, 14H) 2.35 (s, 3H)	Found (Calcd for $C_{20}H_{17}NOS$) C H N 75.32 5.33 4.45 (75.20) (5.36) (4.38)

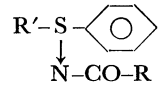
Table 2. Yield of products in the thermal decomposition of I

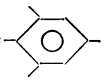
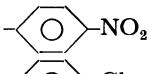
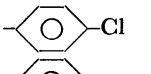
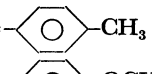
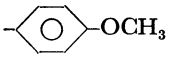
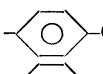
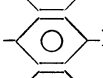
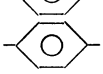
$Ph_2S\rightarrow N-\underset{\underset{O}{\|}}{C}-R \xrightarrow[190\,^\circ C]{\Delta} R-NCO + Ph_2S$

(I) (II)

	R	Bp (mp) (°C)	Yield (%)		IR (cm^{-1})	NMR (δ, $CDCl_3$)
a	Ph	58—59/18 mmHg	34.7[a]	85.7	2270	7.6—6.9 (m, 5H)
b	CH_2Ph	118/200 mmHg	90.4	96.8	2270	7.37 (s, 5H) 4.50 (s, 2H)
c	CHC_2H_5 | Ph		98.8	98.0	2270	7.27 (s, 5H) 4.50 (t, 1H) 2.07—1.50 (m, 2H) 0.97 (t, 3H)
d	Adamantyl	135—136	97.6	98.0	2270	2.30—1.50 (m, 15H)
e	Mesityl	(45—46)	95.5	95.6	2270	6.77 (s, 2H) 2.23 (s, 9H)
f	CH_3	37—38	67.5	91.0	2270	3.03 (s, 3H)

a) Dimerized product of phenyl isocyanate was obtained.

Table 3. Kinetic data of  in DMF

	Sulfilimine		$k\times s^{-1}$	Rel. rate
a	R=Ph	R′=Ph	$1.22\pm0.07\times10^{-4}$ [a]	1.0
b	$R=CH_2Ph$	R′=Ph	$1.25\pm0.12\times10^{-4}$ [b]	7.4
c	$R=CHC_2H_5$ | Ph	R′=Ph	$1.37\pm0.34\times10^{-3}$ [b]	81.6
d	R=Adamantyl	R′=Ph	$4.91\pm0.32\times10^{-4}$ [b]	29.2
e	R= 	R′=Ph	$4.12\pm0.11\times10^{-4}$ [c]	2200
f	R= 	R′=Ph	$1.17+0.09\times10^{-3}$ [b]	69.6
g	$R=CH_3$	R′=Ph	$4.87\pm0.13\times10^{-5}$ [d]	1.1
h	$R=C_2H_5$	R′=Ph	$2.39\pm0.05\times10^{-4}$ [d]	5.3
i	$R=CH(CH_3)_2$	R′=Ph	$9.46\pm0.05\times10^{-4}$ [d]	20.9
j	$R=C(CH_3)_3$	R′=Ph	$7.56\pm0.32\times10^{-4}$ [d]	16.7
k	R= 	R′=Ph	$4.22\pm0.26\times10^{-5}$ [a]	0.35
l	R= 	R′=Ph	$6.10\pm0.31\times10^{-5}$ [a]	0.50
m	R= 	R′=Ph	$4.31\pm0.17\times10^{-5}$ [a]	0.35
n	R= 	R′=Ph	$1.94\pm0.09\times10^{-4}$ [a]	1.6
o	R= 	R′=Ph	$2.36\pm0.05\times10^{-4}$ [a]	1.9
p	R=Ph	R′= 	$2.06\pm0.18\times10^{-4}$ [a]	1.7
q	R=Ph	R′= 	—	
r	R=Ph	R′= 	$0.95\pm0.20\times10^{-4}$ [a]	0.78

a) At 190.8±0.06 °C. b) At 170.3±0.06 °C. c) At 129.2±0.06 °C. d) At 180.25±0.06 °C.

N-acyl-*S*,*S*-arylphenylsulfilimines (Ia—r) was carried out in DMF at around 130—190 °C. The rate of the pyrolysis followed the first order kinetic equation. The dependence of rate on concentration shows that the reaction is of the first order in sulfilimine. The rate constants of the pyrolysis of *N*-acyl-*S*,*S*-arylphenylsulfilimines are summarized in Table 3, together with the relative rates, assuming the rate of the *N*-benzoyl-*S*,*S*-diphenylsulfilimine at 190 °C as the standard. The rate constants can be correlated nicely with the Hammett σ-values, ρ-values of −1.20 (X-substituents) and +0.92 (Y-substituents) being obtained (except *p*-nitro group), (Fig. 1). Pyrolysis of the *p*-nitro derivatives also gave the corresponding isocyanates in low yields and some uncharacterized products. The effect of temperature on the rate is given in Table 4. The activation enthalpies and entropies of both sulfilimines (Ia, e) are calculated to be $\Delta H^{\neq}=38.7$ kcal/mol, $\Delta S^{\neq}=6.0$ e.u. ($E_a=39.5$

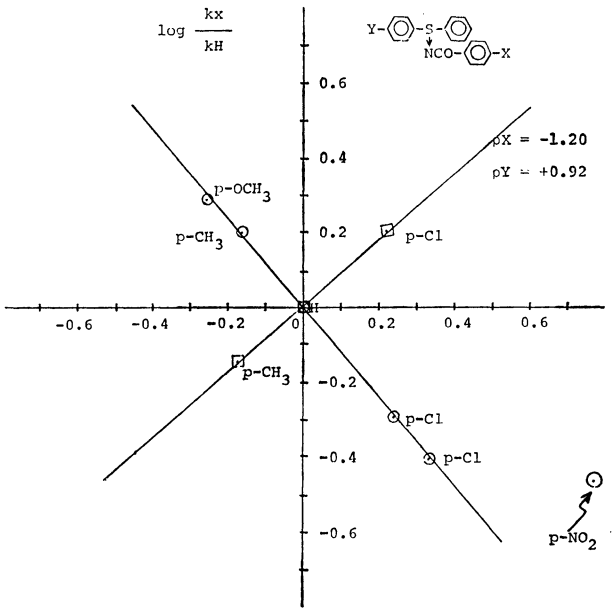


Fig. 1. Hammett plots of *p*- or *m*-substituted sulfilimine.

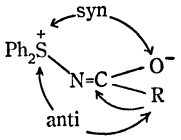
kcal/mol) for Ia, $\Delta H^{\neq}=32.3$ kcal/mol, $\Delta S^{\neq}=5.5$ e.u. ($E_a=33.0$ kcal/mol) for Ie. The effect of solvent on the rate of pyrolysis was examined with *N*-2,4,6-trimethylbenzoyl-*S*,*S*-diphenylsulfilimine in benzene, DMF and ethanol. The results are given in Table 4. The rate increases in a nonpolar aprotic solvent such as benzene but decreases in a polar protic solvent such as EtOH. However, difference in the rate is not large unlike the reaction in which the transition state is more polarized than the ground state.

In contrast to the thermal stability of *N*-tosyl-*S*,*S*-diphenylsulfilimine, *N*-acyl derivatives decompose readily giving the corresponding isocyanates in high yields as shown in Table 2. The facile thermolysis of *N*-acyl-*S*,*S*-diphenylsulfilimines reflects on their IR S–N stretching band which appears at *ca.* 800 cm^{-1} (*e.g.*, *N*-benzoyl-*S*,*S*-diphenylsulfilimine 805 cm^{-1}) and also on that of the carbonyl band of the *N*-acyl group which appears at 1500—1600 cm^{-1} (*e.g.*, *N*-benzoyl-*S*,*S*-diphenylsulfilimine 1595—1535 cm^{-1}). The IR absorptions are in sharp contrast to those of the *N*-tosyl derivatives in which the S–N stretching band appears at 930—970 cm^{-1} (*e.g.*, *N*-tosyl-*S*,*S*-diphenyl, 960 cm^{-1}). A comparison of the S–N bond of the *N*-benzoyl with that of the *N*-tosyl group indicates that the S–N bond of the former can be cleaved more readily. The low frequency shift of the absorption due to the carbonyl group of the *N*-acyl derivatives as compared to the corresponding amide group suggests that the carbonyl bond in the *N*-acylsulfilimines is markedly stretched and the contribution of structure B is greater than that of structure A in the resonance hybrid.

$$Ph_2\overset{+}{S}-\overset{-}{N}-\underset{\underset{O}{\|}}{C}-R \longleftrightarrow Ph_2\overset{+}{S}-N=\underset{\underset{O^-}{|}}{C}-R$$

(A) (B)

X-Ray crystallographic analysis of the *N*-acylsulfilimine indicates structure B to be more favored than structure A (*N*-dichloroacetylsulfilimine)[8] while the S–N–C–O atoms in the molecule are arranged nearly in a coplanar geometry, Ph_2S group and the R group being at the anti arrangement. This molecular



geometry suggests that in *N*-acylsulfilimine, the R group can readily migrate to the imino nitrogen from the back of the leaving group, *i.e.*, diphenyl sulfide, in keeping with the stereochemistry of the Curtius,[9] the Hoffman[10,11] the Lossen,[12] and the Schmidt[13] rearrangements.

The rearrangement of the *N*-acyl-*S*,*S*-arylphenylsulfilimines proceeds *via* simultaneous migration of the R group and cleavage of the S–N bond, since the effect of substituents on the phenyl ring of the migrating group shows a negative ρ-value ($\rho=-1.2$) against Hammett σ-values, while that of the leaving group shows a positive ρ-value ($\rho=+0.92$). The Hammett ρ-values

Table 4. Effect of temperature and solvent on pyrolysis of Ph_2S NCOR (I)

	Sulfilimine (I)	Temp (°C)	$k\times s^{-1}$	γ	$\Delta H^{\neq}$(kcal/mol)	$\Delta S^{\neq}$(e.u.)
a	R=⟨⟩ (DMF)	170.3	$1.68\pm0.09\times10^{-5}$	0.999	38.7	6.0
		180.25	$4.52\pm0.14\times10^{-5}$		(E_a=39.5 kcal/mol)	
		190.8	$1.22\pm0.07\times10^{-4}$			
e	R=⟨⟩- (DMF)	110.3	$5.32\pm0.48\times10^{-5}$	0.994	32.3	5.5
		120.25	$1.32\pm0.05\times10^{-5}$		(E_a=33.0 kcal/mol)	
		129.2	$4.12\pm0.11\times10^{-4}$			
e	R=⟨⟩- (C_6H_6)	102.9	$7.40\pm0.30\times10^{-5}$			
		110.55	$2.01\pm0.15\times10^{-4}$		(E_a=32.9 kcal/mol)	
		121.2	$5.71\pm0.06\times10^{-4}$	0.999	32.1	7.6
e	R=⟨⟩- (EtOH)	121.2	$1.44\pm0.09\times10^{-4}$			
		129.2	$3.31\pm0.30\times10^{-4}$		(E_a=29.72 kcal/mol)	
		139.8	$7.96\pm0.08\times10^{-4}$	0.998	28.9	−3.3

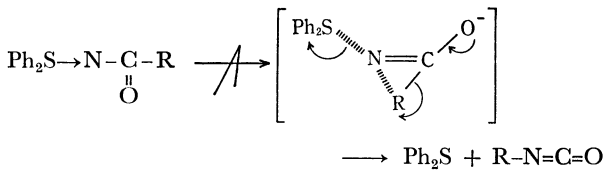
strongly suggest the concerted nature of C–N bond formation and S–N bond breaking in the transition state.

In the [1,2]-shift of the aryl group from carbon to an electron deficient hetero atoms such as nitrogen and oxygen, the Hammett plot with σ^+-values sometimes gives a better correlation than with σ-values.[10,14] However, in the pyrolysis of *N*-acyl-*S*,*S*-arylphenylsulfilimines the Hammett plot can be correlated better with σ-values than σ^+-values except in the NO_2 derivatives. This suggests that the charge separation in the transition state is rather small. This seems to be supported by the fact that the rate of reaction does not increase markedly in polar solvent; the rate of Ie varies from 3.2 in benzene to 1.0 in DMF and to 0.80 in EtOH.

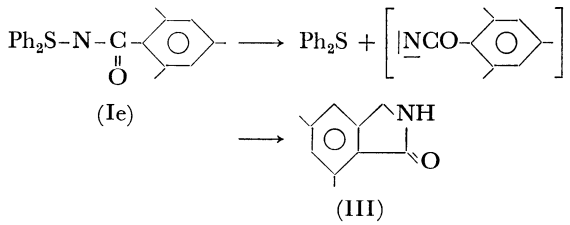
In the pyrolysis of *N*-acyl-*S*,*S*-arylphenylsulfilimines, the migratory aptitude of the alkyl group lies in the order, *tert*≃*sec*>*prim*>Me. As compared to this the phenyl group does not accelerate the rate of rearrangement. This effect on the migratory aptitude is in contrast to other similar rearrangements such as Schmidt,[13] Lossen[12] or Bayer-Villiger[16] reactions. As seen from the data in Table 1, the ortho methyl group accelerates the rate of rearrangement enormously; one *o*-methyl group accelerates 70 times and two *o*-methyl groups increase the rate 2200 times. This is probably due to the steric inhibition of resonance between the phenyl group and N–C or carbonyl group, which prevents the planar conformation of the –NCOR group.[8,17,18] In the *N*-benzoylsulfilimine, the acylamide group would be in the same plane as the phenyl ring, a strong conjugation between the phenyl group and C=O and N=C group retarding the cleavage of the C–Ar bond. Two ortho methyl groups in *N*-2,4,6-trimethylbenzoyl derivative would prevent the conjugation between the phenyl ring and the N–CO– group, facilitating migration of the 2,4,6-trimethylbenzoyl group to the nitrogen atom. The same effect of *o*-substituent was observed in other Curtius type rearrangements.[9]

The activation parameters in the rearrangements are of interest. Despite the large rate difference in the pyrolysis of benzoyl and 2,4,6-trimethylbenzoyl derivatives, the values of activation entropies are similar. Thus, the large rate difference is due solely to that of the enthalpy values. The activation parameters in DMF and benzene are also similar. Similar values of both enthalpies and entropies of activation suggest that the transition states of the rearrangements in both solvents are nearly identical.

All these observations indicate that pyrolysis of the *N*-acyl-*S*,*S*-diphenylsulfilimine proceeds *via* a similar mechanistic path to that of the Curtius rearrangement



Scheme 5.



Scheme 6.

of acid azides involving the rate determining migration of alkyl or aryl group and the concomitant departure of the diaryl sulfide group eventually affording diphenyl sulfide and the isocyanate as shown below.

A similar rearrangement was observed in the photolysis of *N*-acylsulfilimine. The photolysis of *N*-2,4,6-trimethylbenzoyl-*S*,*S*-diphenylsulfilimine affords not only the rearrangement product but also a C–H insertion product which arises *via* the initial formation of a singlet nitrene as shown above. Singlet multiplicity of the nitrene thus generated has also been confirmed by other trapping experiments with an olefin. In the pyrolysis of the sulfilimine, the possibility of the formation of nitrene as intermediate should also be considered. However, no aziridine derivative was detected when pyrolysis of the *N*-benzoyl-*S*,*S*-diphenylsulfilimine in the presence of a large excess of diphenylacetylene was carried out. Furthermore, pyrolysis of *N*-2,4,6-trimethylbenzoylsulfilimine gave neither a trace amount of the inserted product such as 4,6-dimethyl-1-isoindolinone-(III) nor H-abstraction product such as 2,4,6-trimethylbenzoyl amide. Thus the pyrolysis of *N*-acyl-*S*,*S*-diphenylsulfilimines does not seem to involve the initial formation of a nitrene from which alkyl or aryl group migrates subsequently to afford the isocyanates but is considered to be a concerted process. The yields of both the isocyanate and diaryl sulfide are much higher in the pyrolysis than the photolysis of the same *N*-acyl-*S*,*S*-diarylsulfilimine. Thus, pyrolysis is a convenient method for preparation of isocyanates.

Experimental

Preparation of N-*Acyl*-S,S-*arylphenylsulfilimine.* *N*-Acyl-*S*,*S*-arylphenylsulfilimines were prepared according to the known method starting from free *S*,*S*-arylphenylsulfilimines and appropriate acylating agents. A typical example is shown below.

N-*2,4,6-Trimethylbenzoylsulfilimine.* Free *S*,*S*-diphenylsulfilimine (1.0 g, 4.98 mmol) was dissolved in 5 ml benzene. To this was added 1.1 g (5.99 mmol) of 2,4,6-trimethylbenzoyl chloride in 5 ml benzene at room temperature. Benzene was removed *in vacuo* and the residual solid was recrystallized from benzene–hexane. *N*-2,4,6-Trimethylbenzoyl-*S*,*S*-diphenylsulfilimine 0.9 g was obtained in 52.0% yield, mp 143—144 °C. Other *N*-acyl-*S*,*S*-arylphenylsulfilimines were similarly prepared. Their yields, spectral data and elemental analyses are given in Table 1.

Pyrolysis of N-*Acyl*-S,S-*arylphenylsulfilimine.* The pyrolysis of *N*-acyl-*S*,*S*-arylphenylsulfilimine was carried out *in situ* or such solvents as DMF, benzene, tetralin at *ca.* 120—200 °C for 0.3—3 h. A typical experiment is shown below.

Pyrolysis of N-*2,4,6-Trimethylbenzoyl*-S,S-*diphenylsulfilimine.* The sulfilimine, 60 mg, was heated in a sealed tube *in situ* at 190 °C for 20 min. After the usual work-up, diphenyl sulfide

and 2,4,6-trimethylbenzoyl isocyanate were obtained quantitatively by gas chromatography. 2,4,6-Trimethylbenzoyl isocyanate was isolated by GLC (TCD column SE-30, 2 m×2 mm, column temp 130 °C, He 1.6 kg/cm²) in 95.5% yield. All the isocyanates thus obtained are summarized in Table 2 together with their spectral data.

Kinetics of N-*Acyl*-S,S-*arylphenylsulfilimine*. A typical kinetic procedure is as follows; to a 0.1 mol/l solution of *N*-acyl-*S*,*S*-arylphenylsulfilimine in DMF, benzene and ethanol (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 the desired temperature. 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, it was shaken vigorously for a while. The hexane layer was then separated and 2 μl of the hexane solution was injected directly into a gas chromatography column. Gas chromatography was carried out under the following conditions; column SE-30, 1 m×2 mm, column temp 140 °C, He 0.7 kg/cm². The rate constants of the reaction were calculated by the first order kinetic equation, where a concentration change of diphenyl sulfide is calculated from the relative peak-height of benzyl phenyl sulfide (internal standard) each time. The activation parameters were calculated as usual and the Hammett plots were made against σ-values. The data obtained are summarized in Tables 3 and 4 and Fig. 1.

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