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DIPHENYL N-HALOSULFILIMINES

PREPARATION, DECOMPOSITION, AND REACTIONS WITH NUCLEOPHILES'

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Abstract—Diphenyl N-chloro-(**1**), N-bromo-(**2**) and N-iodo-sulfilimines (**3**) were prepared by halogenation of diphenyl free sulfilimine. Compound **1** decomposed in benzene at room temperature. The decomposition of **1** is a chain reaction since the reaction was induced by chlorine or t-butyl hypochlorite affording diphenyl(diphenylsulfilimino) sulfonium chloride(**4a**), while it was inhibited by styrene or stilbene. Compound **4a** was also obtained by the reaction of **1** with diphenyl sulfide in benzene. Decomposition of **1** in acetic acid proceeded smoothly affording various products. Compound **1** reacted with sulfides, sulfoxides, triarylphosphines and triethylamine affording the N-substituted iminosulfonium salts. Compounds **1** and **2** were hydrolyzed with sodium hydroxide affording diphenyl sulfoximine. The reaction of **1** with sodium cyanide gave diphenyl N-cyanosulfilimine(**17**). The reaction of **1** with Grignard reagent gave diphenyl free sulfilimine. Compounds **2** and **3** are more stable than **1**. Decomposition of **2** in benzene or acetic acid gave diphenyl(diphenylsulfilimino)sulfonium perbromide(**4c**).

The chemistry of sulfilimines(iminosulfuranes) has been explored mostly with N-acyl derivatives. Recently, we found a simple procedure to prepare "free" sulfilimine (RSR') by treating N-*p*-tosylsulfilimines with conc. sulfuric acid,[2,3] and opened up a new field of chemistry. Earlier, free sulfilimines have been considered unstable and to decompose readily at room temperature.[4,5] Indeed, this is true with alkyl free sulfilimines but diaryl free sulfilimines are quite stable and easy to handle and may be useful for syntheses of other sulfilimine derivatives. A variety of diaryl N-acylsulfilimines were prepared from diphenyl free sulfilimine with acylating agents.[3,6,7] Also, the N-halogen substituted sulfilimines may be interesting, since they can produce various sulfilimine derivatives.

Diphenyl free sulfilimine was reacted with halogenating agents, and diphenyl N-halosulfilimines were readily prepared as relatively stable compounds.[8] The N-halogen substituted sulfoximines[9,10] react with sulfide or phosphine affording either the sulfonium or phosphonium derivatives. Diphenyl N-halosulfilimines also react not only with such soft nucleophiles as sulfides, phosphines and tertiary amines, but also with hard nucleophiles as hydroxides and amides to give both interesting and useful compounds.

This paper deals with the synthesis and chemical behaviour of diphenyl N-halosulfilimines.

RESULTS AND DISCUSSION

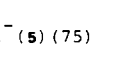
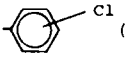
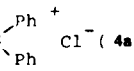
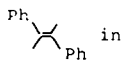
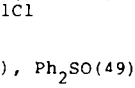
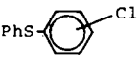
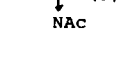
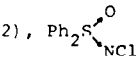
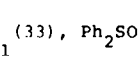
Diphenyl N-chlorosulfilimine(**1**)

Decomposition of **1**. Compound **1** was obtained as pale yellow crystals by the chlorination of diphenyl free sulfilimine with N-chlorosuccinimide or by treatment of the sulfuric acid salt of diphenyl free sulfilimine with sodium hypochlorite. Compound **1** decomposed gradually at room temperature or upon exposing to air for 20 days, affording diphenyl free sulfilimine hydrochloride (**5**) in 75% yield. More than 1 g of **1** sometimes decomposed explosively when it was kept for several hours at room temperature. The pyrolysis of **1** was more facile (neat, 90°, 1.5 hr) than the corresponding free sulfilimine (100°, 5 hr)[2,3] and gave diphenyl sulfide as a major product. The decomposition of **1** took place more readily in any solvent and the products and their yields were changed by changing the solvent used. The results are summarized in Table 1.

When a benzene solution of **1** was kept for several hours at room temperature, the solution suddenly became muddy and evolved an irritating gas and solid **4a** precipitated simultaneously. The gas evolved was not analyzed in detail, but it seemed to be a mixture of N_2, Cl_2 and HCl. Decomposition of **1** in chloroform solution also took place vigorously but in acetic acid the reaction proceeded smoothly with the evolution of gas, precipitating ammonium chloride and eventually affording various products. The decomposition of **1** in methanol solution, proceeded slowly without evolving gas, and crystalline diphenyl N-chloro-sulfoximine precipitated. The structure of **4a**[11] was determined by IR, NMR, elemental analyses and the following chemical reactions:

Compound **4a** is very hygroscopic and did not give a constant m.p. and was therefore, converted to its perchlorate salt. When the hydrolysis of **4a** was carried out under alkaline condition, it afforded both diphenyl sulfoxide and diphenyl free sulfilimine in good yields. Compound **4a** was also obtained by the reaction of **1** with diphenyl sulfide in benzene. If wet benzene was used, the corresponding sulfoxide and the salt **5** were obtained instead of **4a** suggesting that the reaction of **1** with diphenyl sulfide does not proceed simply via the nucleophilic substitution of Cl on the N atom by sulfide. The decomposition of **1** in benzene was quickly initiated by Cl gas and t-butyl hypochlorite, and inhibited by olefins (i.e. styrene, stilbene). In the presence of stilbene, **1** decomposed slowly affording meso - 1,2 - dichloro - 1,2 -

Table 1. Decomposition of diphenyl N-chlorosulfilimine(**1**)

Conditions	Products and Yields(%)
in the air r.t. 20 days	 (**5**)(75)
neat 90° 1.5 hr	PhSPh(52), HCl,  (trace)
in C_6H_6 r.t. 24 hr	 (**4a**)(74), PhSPh(12) Ph_2SO(20)
 in C_6H_6 r.t. 10 days	meso-  (20), Ph_2SO(23), **5**(45)
in $CHCl_3$ r.t. 24 hr	PhSPh(22), Ph_2SO(49), NH_4Cl(23), **4a**(6), **5**(4)
in AcOH r.t. 2 days	**4a**(15), PhSPh(4),  (6), NH_4Cl(40), Ph_2SO_2(50), Ph_2SO(6),  (9)
in MeOH r.t. 7. days	 (12),  (33), Ph_2SO(trace)

diphenylethane together with diphenyl sulfoxide and **5**. Apparently the decomposition of **1** in benzene should be initiated by some species formed during the reaction (i.e. Cl_2; like an induced decomposition).

The chain process may follow either one of the following mechanistic routes (Fig. 1).

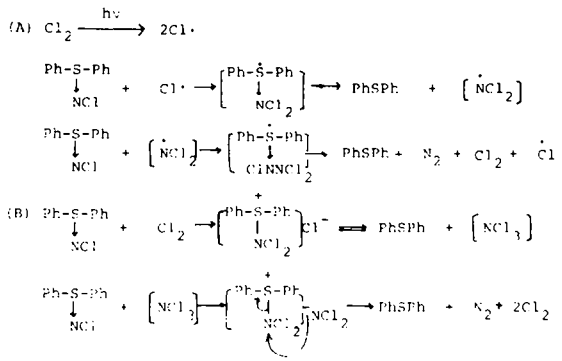


Fig. 1.

Path A is a radical chain process, and would not be unreasonable, for we reported earlier that N-*p*-tosylsulfilimine was reduced by the tin radical.[12]

Path B is an ionic chain reaction in which the chain carrier is molecular chlorine and trichloramine. The formation of trichloramine is a reversal step of the reaction of diphenyl sulfide with trichloramine affording **4a**.[11] The **4a** is considered to be formed through a route in which diphenyl sulfide formed during the decomposition is incipiently chlorinated with **1** giving an intermediate chlorosulfonium salt which is then immediately substituted by the counter anion as shown below. (Fig. 2). In the presence of water, the salt should yield the sulfoxide and **6**.

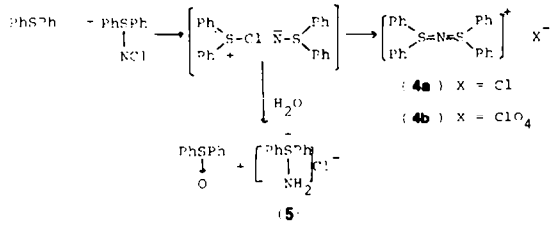


Fig. 2.

If the reaction proceeds via path B, the amount of chain carrier chlorine molecules should accumulate gradually during the decomposition and hence the reaction should proceed explosively.

Reactions of **1** *with sulfides, sulfoxides, triarylphosphines and triethylamine.* Appel *et al.* reported that the reaction of N-halosulfoximines or N-halosulfone diimines with sulfides or phosphines afforded the corresponding onium salts.[9] Decomposition of **1** to **4a** indicates that N-halosulfilimines also react with sulfides. The products of the reaction of **1** with sulfides, sulfoxides, triarylphosphines and triethylamine are shown in Table 2, and IR, NMR and elemental analyses are shown in Table 6.

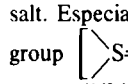
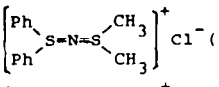
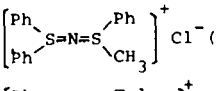
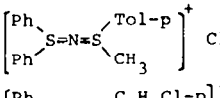
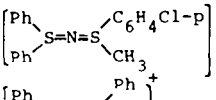
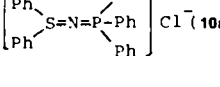
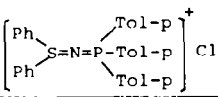
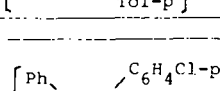
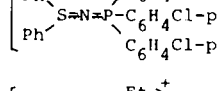
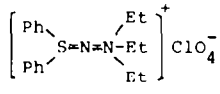
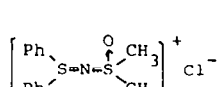
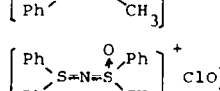
These compounds are the sulfilimine derivatives stabilized by electronegative hetero atoms, and isoelectronic to the sulfilimine rather than the aminosulfonium salt. Especially, **4a** and the analogues which contain the group  are a new class of sulfur compounds.[11,13-15] Griffin and Sheldrick[16] determined the structure of what appears to be dimethyl (dimethylsulfilimino)sulfonium bromide by X-ray diffraction, and the S–N bond length and S–N–S angle were found to be 1.64, 1.63 Å and 110.8° respectively. These values are very

Table 2. Reactions of diphenyl N-chlorosulfilimine(**1**) with sulfides, sulfoxides, phosphines and triethylamine

Reactions	Conditions	Products and Yields(%)(mp°)
PhSPh	in C_6H_6 r.t. 5 hr	PhSPh (O) (30), **5**(21), **4a**(65)(172-2.5)[a]
CH_3SCH_3	in C_6H_6 r.t. 24 hr	 Cl^- (**6**)(99)(160-1)[a]
$PhSCH_3$	in C_6H_6 r.t. 24 hr	 Cl^- (**7**)(82)(107.5-8)[a]
p-$TolSCH_3$	in C_6H_6 r.t. 0.5 hr	 ClO_4^- (**8**) (58)[b] (121-2)[a]
p-$ClC_6H_4SCH_3$	in C_6H_6 r.t. 1 hr	 ClO_4^- (**9**)(39)[b] (143-4)[a]
Ph_3P	in C_6H_6 r.t. 2 hr	 Cl^- (**10a**)(91)(311)(**10b**)[b] (43)
$(p\text{-}Tol)_3P$	in C_6H_6 r.t. 0.5 hr	 ClO_4^- (**11**)(54)[b] (>250)
$(p\text{-}ClC_6H_4)_3P$	in C_6H_6 r.t. 0.5 hr	 ClO_4^- (**12**)(73)[b] (>250)
Et_3N	in C_6H_6 r.t. 24 hr	 ClO_4^- (**13**)(93)(128-9)[a]
CH_3SCH_3 (O)	neat r.t. 20 hr	 Cl^- (**14**)(54)(195-6(dec.))
$PhSCH_3$ (O)	neat r.t. 24 hr	 ClO_4^- (**15**)(23)[b] (oil)
p-$TolSCH_3$ (O)	neat r.t. 24 hr	 ClO_4^- (**16**)(43)[b] (oil)

a) mp as perchlorates b) The salt formed was converted to its perchlorate and the yiled is shown as the perchlorate.

similar to those of dimethyl N-methanesulfonylsulfilimine ($Me_2S \rightarrow N\text{-}SO_2Me$, S→N 1.63, S-N 1.58 Å, S-N-S 116°).[17] The structure of these cation species may best be represented by the following formula: $Me_2\dot{S}\text{=}N\text{-}\dot{S}Me_2 \leftrightarrow Me_2\dot{S}\text{-}N\text{-}\dot{S}Me_2 \leftrightarrow Me_2\dot{S}\text{-}N\text{=}SMe_2 \leftrightarrow Me_2S\text{=}\dot{N}\text{=}SMe_2$, in which the major contribution derives from the second structure which has two lone pairs on N and one on each S atom. Our present data seem to indicate that **4a** is similar to the aminosulfonium salt.[18] For example, **4a** was hydrolyzed by sodium hydroxide, giving diphenyl sulfoxide and diphenyl free sulfilimine. However, diphenyl free sulfilimine or diphenyl N-*p*-tosylsulfilimine is stable under alkaline conditions.[2,3,19] As shown in Table 2, N-chlorosulfilimine reacts with tertiary amines and sulfoxides. Therefore **1** is more reactive than chloramine-T which does not react with sulfoxides except DMSO, without copper catalysis.[20] The product from the sulfoxide (**14**-**16**) was hydrolyzed more readily than **4a**. For example, **15** was hydrolyzed with aqueous sodium hydroxide affording diphenyl sulfoxide (81%) and methyl phenyl sulfoximine (80%). Therefore, the compound behaves like an aminosulfonium salt. Meanwhile, **10b** was also hydrolyzed with sodium hydroxide, affording triphenylphosphine oxide and diphenyl free sulfilimine, but the product formed with triethylamine **13** was not hydrolyzed with sodium hydroxide in refluxing methanol even after 15 hr.

Table 3. Reactions of **1** with nucleophiles

Reagents	Conditions	Products and Yields(%)
NaCN	in CH_3OH r.t. 12 hr	PhSPh (NCN) (**17**) (4), PhSPh (NH) (39)
NaCN	in DMSO r.t. 12 hr	**17** (50), PhSPh (NH) (15)
NaOH	in CH_3OH 45° 12 hr	PhSPh (O, NH) (96)
p-TolMgBr	in THF r.t. 12 hr	PhSPh (13), PhSPh (NH) (65)

Reactions of **1** *with other nucleophiles*

Reactions of **1** with sodium cyanide, sodium hydroxide and *p*-tolylmagnesium bromide are shown in Table 3.

The results seem to indicate that the nucleophiles can attack either one of the three cationic centers namely sulfur, nitrogen or chlorine. The reaction with cyanide proceeds either via the direct substitution on the N atom or by the initial attack on chlorine affording cyanogen chloride, followed by the attack by the sulfilimino nitrogen forming N-cyanosulfilimine[21] as shown in Fig. 3. The present results alone cannot disclose the actual mechanism.

In the reaction with *p*-tolyl Grignard reagent, the anionic *p*-tolyl species appears to attack the Cl atom, and the reaction stops at the first step to form the sulfilimino magnesium bromide[22] (Fig. 4).

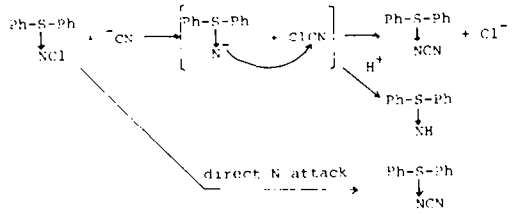


Fig. 3.

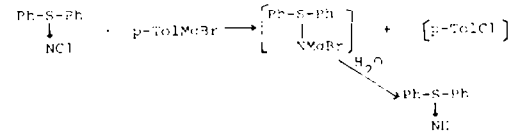
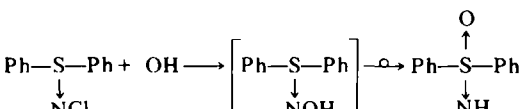
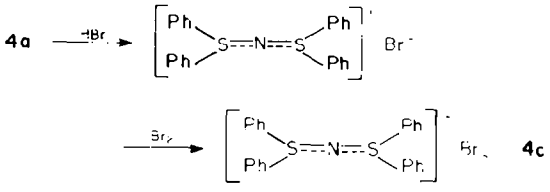


Fig. 4.

In the case of hydroxide anion, although the actual mechanism is not known, probably the initially formed N-hydroxysulfilimine may rearrange to afford the thermodynamically more stable sulfoximine as shown below.[23]



Diphenyl N-*bromosulfilimine*(**2**). Compound **2** was prepared as yellow crystals by bromination of diphenyl free sulfilimine with N-bromosuccinimide. It is more stable than **1** and can be stored for a month without serious decomposition even after exposure to air and light. Unlike **1**, decomposition of **2** in benzene proceeded slowly affording diphenyl(diphenylsulfilimino)sulfonium perbromide (**4c**) whose structure was determined by the elemental and spectroscopic analyses and the following chemical reactions. When **4a** was treated with hydrobromic acid and then with an excess of bromine, **4c** was obtained quantitatively.



Reaction of **2** with methyl phenyl sulfide in the presence of water afforded methyl phenyl sulfoxide and diphenyl amino-sulfonium bromide together with methylphenyl (diphenylsulfilimino) sulfonium bromide. As in the case of **1**, the reaction appears to take place not on the N atom but on the Br atom forming bromosulfonium salt as an initial intermediate. Decomposition of **2** in acetic acid gave **4c** spontaneously when it was dissolved into the acid. Compound **2** also reacted with alkali affording the corresponding sulfoximine. The results are summarized in Table 4.

Diphenyl N-*iodosulfilimine*(**3**). Compound **3** was prepared as yellow crystals by the reaction of diphenyl free sulfilimine with iodine and sodium hydroxide and it is also more stable than **1**.

EXPERIMENTAL

Diphenyl N-*chlorosulfilimine*(**1**). Diphenyl free sulfilimine[2,3] (1.0 g) and N-chlorosuccinimide (0.67 g) were dissolved in 5 ml acetone cooling in cold water. The soln was poured into cold water and the oily substance solidified immediately The ppt was collected, washed with water and dried, yield was 1.07 g (100%), m.p. 116–7° (dec) from benzene–hexane. (Found: C, 61.19; H, 3.92; N, 6.07. Calc. for $C_{12}H_{10}SNCl$: C, 61.14; H, 4.28; N, 5.94%), IR (KBr) cm^{-1} 860 (SN), NMR ($CDCl_3$) δ ppm 7.52 (s, phenyl).

Another method. Diphenyl free sulfilimine (1.0 g) was dissolved in 5 ml 5% H_2SO_4 aq to which was added 5 ml of 10% NaOCl aq at 0°. The ppt was treated similarly and the **1** obtained was used for further reactions immediately.

Diphenyl N-*bromosulfilimine*(**2**). Diphenyl free sulfilimine (1.0 g) and N-bromosuccinimide (0. 9 g) were dissolved in 5 ml acetone. The same treatment as above afforded **2** as yellow crystals quantitatively, m.p. 96–7°, (dec) from benzene–hexane. (Found: C, 51.87; H, 3.33; N, 5.02. Calc. for $C_{12}H_{10}SNBr$: C, 51.44; H, 3.60; N, 5.00%), IR (KBr) cm^{-1} 860 (SN), NMR ($CDCl_3$) δ ppm 7.55 (s, phenyl).

Table 4. Products and yields for the reaction of diphenyl N-bromosulfilimine(2)

Conditions	Products and Yields(%)
in C_6H_6 r.t. 20 days	PhSPh(56), **4c**(89)
in AcOH r.t. 12 hr	PhSPh, **4c**(quant.)
$PhSCH_3$ in $C_6H_6(H_2O)$ r.t. 24 hr	PhSPh(8), $PhSCH_3$(O)(36), $[PhSPh(NH_2)]^+Br^-$(16), $[(Ph)_2S{=}N{=}S(Ph)_2]^+Br^-$(63)
NaOH in CH_3OH 45° 15 hr	Ph-S(=O)(=NH)-Ph(70)

Diphenyl N-iodosulfilimine(**3**). Diphenyl free sulfilimine (0.02 g). NaOH (0.04 G) and I_2 (0.23 g) were dissolved in 3 ml MeOH under cooling with ice. The soln was poured into ice water and the oily substance solidified immediately. The ppt was collected, washed with water and dried. Yellow crystals were obtained quantitatively, m.p. 99–100°(dec) from benzene–hexane. (Found: C, 43.87; H, 2.89; N, 4.19. Calc. for $C_{12}H_{10}SNI$: C, 44.05; H, 3.08; N, 4.28%), IR (KBr) cm^{-1} 880 (SN), NMR ($CDCl_3$) δ ppm 7.57.

Decomposition of **1** *in air.* Compound **1** (50 mg) was kept in contact with air at room temp. for 20 days. The crystals changed to a white powder, which was recrystallized from chloroform-acetone affording **5** in 75% yield, m.p. 155–6.5°, IR (KBr) cm^{-1} 3080, 2950, 2690, 745; NMR ($CDCl_3$) δ ppm 7.4–7.7 (6 H, m, phenyl-*meta* and *para*), 7.8–8.1 (4 H, m, phenyl-*ortho*), 8.30 (2 H, s, NH_2). If wet crude **1** was kept for 2 days at room temp., **1** was converted to the corresponding sulfone completely. When **5** was dissolved in water, and the soln made alkaline, diphenyl free sulfilimine was obtained. In addition, **5** was prepared from free sulfilimine and HCl in the following manner. Diphenyl free sulfilimine (1 g) was dissolved in 1.4 ml of 10% HCl under cooling with ice, filtered, and the filtrate was concentrated *in vacuo*, and to this was added 10 ml acetone. The ppt was filtered off, dried, and recrystallized from chloroform-acetone, m.p. 154–6°. (Found: C, 60.64; H, 5.14; N, 5.98 Calc. for $C_{12}H_{12}NSCl$: C, 60.62; H, 5.09; N, 5.89%).

General methods of decomposition of diphenyl N-chlorosulfilimine(**1**). Generally, 100–200 mg of **1** was used for the decomposition under various conditions shown in Table 1. All the products were separated by column chromatography using silica gel, and identified by IR, NMR, GLC and elemental analyses.

Diphenyl(diphenylsulfilimino)sulfonium chloride(**4a**). Compound **4a** formed by the decomposition in benzene was hygroscopic and did not give a constant m.p. (lit.[11] 80° dihydrate, 181–2° (dec) anhyd). Therefore, **4a** was converted to its perchlorate salt **4b** by adding sodium perchlorate to an aqueous soln, m.p. 172–215° (from chloroform-ether), IR, NMR and elemental analyses are shown in Tables 5 and 6.

Alkaline hydrolysis of **4a**. Compound **4a** (60 mg) and 1.5 ml 20% NaOH aq in 2 ml MeOH was heated in a sealed tube at 70° for 5 hr. The soln was poured into 5 ml cold water and extracted with chloroform. The chloroform layer was separated and extracted with 1% H_2SO_4aq. From the chloroform layer 25 mg diphenyl sulfoxide was obtained (87%), and the aqueous layer was then made alkaline, extracted with chloroform, and 25 mg diphenyl free sulfilimine was obtained (80%).

Reaction of **1** *with diphenyl sulfide.* Compound **1** (100 mg) was dissolved in 2 ml benzene, to which was added diphenyl sulfide (87 mg) at room temp. After 5 min, the benzene was removed *in vacuo*, and the residue chromatographed through a column packed with silica gel. Diphenyl sulfoxide (26 mg, 30%), **4a** (116 mg, 65%) and **5** (21 mg, 21%) were obtained.

Table 5. Elemental analyses of $[Ph_2S\text{-}N\text{-}X]^+Y^-$

X	Y	Analytical Data
PhSPh	ClO_4	Found C; 58.77, H; 4.00, N; 2.68
		Calcd. C; 59.31, H; 4.15, N; 2.88
CH_3SCH_3	ClO_4	Found C; 46.25, H; 4.41, N; 3.99
		Calcd. C; 46.47, H; 4.46, N; 3.87
$PhSCH_3$	ClO_4	Found C; 53.93, H; 4.23, N; 3.41
		Calcd. C; 53.83, H; 4.28, N; 3.30
p-TolSCH$_3$	ClO_4	Found C; 54.55, H; 4.54, N; 3.08
		Calcd. C; 54.41, H; 4.57, N; 3.17
p-$ClC_6H_4SCH_3$	ClO_4	Found C; 49.82, H; 3.69, N; 2.79
		Calcd. C; 49.79, H; 3.74, N; 3.06
Ph_3P-	Cl	Found C; 71.90, H; 4.99, N; 2.59
		Calcd. C; 72.35, H; 5.06, N; 2.81
Et_3N-	ClO_4	Found C; 53.63, H; 6.11, N; 6.98
		Calcd. C; 53.92, H; 6.29, N; 6.99

Diphenyl N-chlorosulfoximine. Diphenyl sulfoximine (100 mg)[3,24] and N-chlorosuccinimide (67 mg) dissolved in 1 ml acetone, yielded, as in the case of **1**, a compound m.p. 149.5–150.0° from benzene–hexane, IR (KBr) cm^{-1} 965, 1090, 1235, identical with those of diphenyl N-chlorosulfoximine obtained by the decomposition of **1** in MeOH.

Decomposition of **1** *in the presence of stilbene.* Compound **1** (100 mg) and *trans*-stilbene (153 mg) was dissolved in 3 ml benzene, and the soln was kept for 10 days at room temp. Crystalline **5** slowly precipitated and was filtered off. The filtrate was condensed and the residue was chromatographed through a column packed with silica gel. The products shown in Table 1 were *meso*-1,2-dichloro-1,2-diphenylethane: m.p. 191–2°, (20%), diphenyl sulfoxide (23%) and **5** (45%).

Reaction of **1** *with sulfides.* In general, **1** (0.10 g) was dissolved in 2 ml benzene, to which was added 1.2 molar amounts of sulfides shown in Table 2. Compounds **6** and **7** were purified by silica gel column chromatography, and then converted to the corresponding perchlorates by adding aqueous sodium perchlorate. In the case of other methyl aryl sulfides, the benzene soln was decanted off after the reaction, and the oily products were washed with benzene, dissolved in 2 ml water and treated with charcoal. To this was added an excess sodium perchlorate. IR, NMR and elemental analyses of the products are summarized in Tables 5 and 6.

Reaction of **1** *with sulfoxides.* Compound **1** (0.24 g) was added to methyl phenyl sulfoxide (1.4 g) and the mixture was stirred for 24 hr at room temp. Excess ether was added, and the oily products were washed with ether. The products were dissolved in 2 ml water, to which was added excess sodium perchlorate and stirred for 5 hr at room temp. Subsequently, the aqueous soln was

Table 6. IR and NMR spectra of $[Ph_2S\text{-}N\text{-}X]^+Y^-$

X	Y	I.R. (cm^{-1})			N.M.R. ($CDCl_3$) δ ppm	
			ν_{SN}	other	phenyl	other
PhSPh	Cl	KBr	930	3400 (H_2O)	7.64–7.86 (8H, m, ortho) 7.33–7.64 (12H, m, meta and para)	
PhSPh	ClO_4	KBr	900	1095 (ClO_4)	7.22–7.70 (m)	
CH_3SCH_3	Cl	neat	910	3470 (H_2O)	7.3–7.8 (10H, m)	3.09 (6H, s, CH_3) 3.80 (4.8H, s, H_2O)
CH_3SCH_3	ClO_4	KBr	890 920	1080 (ClO_4)	7.60 (10H, s)	2.93 (6H, s, CH_3)
$PhSCH_3$	Cl	neat	910	3500 (H_2O)	7.3–8.0 (15H, m)	3.46 (3H, s, CH_3)
$PhSCH_3$	ClO_4	KBr	910	1085 (ClO_4)	7.30–7.85 (15H, m)	3.21 (3H, s, CH_3)
p-$TolSCH_3$	ClO_4	KBr	920	1085 (ClO_4)	7.30–7.90 (14H, m)	3.20 (3H, s, CH_3) 2.35 (3H, s, CH_3)
p-$ClC_6H_4SCH_3$	ClO_4	KBr	940	1085 (ClO_4)	7.3 –7.90 (14H, m)	3.21 (3H, s, CH_3)
Ph_3P-	Cl	KBr		1060, 1115	7.3–7.9 (m)	
Ph_3P-	ClO_4	KBr		1120, 1060, 1000 1090 (ClO_4)	7.4–7.9 (m)	
$(p\text{-}Tol)_3P$-	ClO_4	KBr		1100, 1000, 1085 (ClO_4)	7.3–7.9 (22H, m)	2.44 (9H, s, CH_3)
$(p\text{-}ClC_6H_4)_3P$-	ClO_4	KBr		1100, 1000, 1085 (ClO_4)	7.4–7.9 (22H, m)	
Et_3N-	Cl	neat		3430 (H_2O)	7.64–7.85 (4H, m, ortho) 7.30–7.64 (6h, m, meta and para)	3.69 (6H, q, CH_2)
Et_3N-	ClO_4	KBr		1080 (ClO_4)	7.60–7.82 (4H, m, ortho) 7.35–7.60 (6H, m, meta and para)	3.54 (6H, q, CH_2) 1.20 (9H, t, CH_3)
$CH_3\overset{\uparrow O}{S}CH_3$	Cl	KBr		980, 1220, 1050 (NSO)	7.5–8.0 (10H, m)	3.87 (6H, s, CH_3)
$PhS\overset{\uparrow O}{C}H_3$	ClO_4	neat		950, 1020, 1240 (NSO) 1085 (ClO_4)	7.4–8.1 (15H, m)	3.80 (3H, s, CH_3)
p-$TolS\overset{\uparrow O}{C}H_3$	ClO_4	neat		1240, 1030, 1000 (NSO) 1085 (ClO_4)	7.3–8.0 (14H, m)	3.78 (3H, s, CH_3) 2.44 (3H, s, CH_3)

extracted with chloroform, and the chloroform layer dried over $MgSO_4$, and the chloroform evaporated under reduced pressure. The residue was chromatographed through a column packed with silica gel using chloroform–methanol (10:1, v/v) as an eluent. Compound **15** (0.10 g, 23%) and **4b** (20 mg, 8%) were obtained. Similarly, the reaction of **1** with dimethyl sulfoxide or methyl *p*-tolylsulfoxide was carried out, and products, yields, IR, NMR and elemental analyses are summarized in Tables 2, 5 and 6.

Reaction of **1** *with triarylphosphines.* Compound **1** (0.10 g) was dissolved in 2 ml benzene, and to this was added a 1 ml benzene soln of triphenylphosphine (0.12 g) yielding a crystalline product immediately. After 2 hr, **10a** was obtained by filtration (0.19 g, 91%) and recrystallized from MeOH–ether. Similarly tri(*p*-tolyl)phosphine or tri(*p*-chlorophenyl)phosphine was treated with **1**, and the salt obtained was converted to the corresponding perchlorate. The results are shown in Tables 2, 5 and 6.

Reaction of **1** *with triethylamine.* Compound **1** (0.10 g) was dissolved in 1 ml benzene, to which was added triethylamine (0.5 g) and the soln was kept at room temp. for 24 hr. After the reaction, the crystalline hygroscopic product was obtained by decantation of benzene, and converted to non-hygroscopic perchlorate salt. The results are shown in Tables 2, 5 and 6.

Alkaline hydrolysis of diphenyl(methylphenylsulfoximino)-sulfonium perchlorate(**15**). Compound **15** (80 mg) and 2 ml 20% NaOH aq was dissolved in 3 ml MeOH and the soln was stirred at room temp. for 3 hr. After the reaction, the soln was diluted with water and extracted with chloroform. The chloroform layer was extracted with 0.1 N HCl 3 times. From the chloroform layer, diphenyl sulfoxide (26 mg, 81%) was obtained. The aqueous layer was then made alkaline, and extracted with chloroform. Methyl phenyl sulfoximine[24] (25 mg, 80%) was obtained. Both products were identified by IR and NMR.

Alkaline hydrolysis of diphenyl(triphenylphosphinimino)-sulfonium perchlorate(**10b**). Compound **10b** (0.14 g) and 0.5 ml 20% NaOH aq was dissolved in 5 ml EtOH, and the soln was refluxed for 2 hr. Then, the mixture was poured into ice-water, and extracted with chloroform. The chloroform layer was extracted with 0.1 N HCl 3 times. The chloroform layer was dried over $MgSO_4$. After the chloroform was evaporated under reduced pressure, the residue was chromatographed through a column packed with silica gel. Triphenylphosphine oxide was obtained quantitatively. The aqueous layer was then made alkaline, extracted with chloroform. Diphenyl free sulfilimine (50 mg, 91%) was obtained. Both products were identified by comparing their IR and m.p. with those of the authentic samples.

Alkaline hydrolysis of triethyl(diphenylsulfilimino)ammonium perchlorate(**13**). Compound **13** (0.18 g) was dissolved in 10 ml MeOH, to which was added 1 ml 20% NaOH aq and the soln was refluxed for 2 hr. After the usual work up, the starting material was recovered quantitatively. The same soln of **13** was refluxed for 15 hr, however no reaction occurred (83% recovered).

Reaction of **1** *with sodium cyanide.* Compound **1** (0.20 g) and anhyd NaCN (51 mg) was dissolved in 3 ml MeOH, and the soln was kept for 12 hr at room temp., then the soln was poured into cold water and extracted with chloroform. The chloroform layer was separated and extracted with 1% H_2SO_4 aq. The chloroform layer was condensed and the residue was chromatographed through a column packed with silica gel. Compound **17** (7 mg, 4%) was obtained. The aqueous layer was made alkaline, and extracted with chloroform. Diphenyl free sulfilimine (73 mg, 39%) was obtained. In addition, **17** was prepared by Swern's method[21] and the IR and m.p. were the same as that obtained from **1**. Similarly, **1** was reacted with NaCN in DMSO, and the results are shown in Table 3.

Reaction of **2** *with methyl phenyl sulfide in the presence of a small amount of water.* Compound **2** (0.56 g) and methyl phenyl sulfide (0.248 g) was dissolved in 10 ml benzene containing 5% water, and the soln was stirred at room temp. for 24 hr. After the reaction the solvent was evaporated. The residue was extracted with chloroform, and the soln was dried over $MgSO_4$. The chloroform was evaporated and the residue was chromatographed through a column packed with silica gel using chloroform as an eluent. The results are shown in Table 4.

Reaction of **1** with *p-tolylmagnesium bromide.* Compound **1** (0.20 g) was dissolved in 5 ml anhyd THF. To this was added a 5 ml soln of *p*-tolylmagnesium bromide prepared from *p*-bromotoluene (0.29 g) and Mg (41 mg) in 5 ml anhyd THF. The soln was then kept at room temp. for 12 hr. After the reaction, the soln was decomposed with water, extracted with chloroform, and the chloroform layer was extracted with 0.1 N HCl. The chloroform layer was dried over Na_2SO_4, after the evaporation of chloroform, the residue was chromatographed. From the HCl layer, diphenyl free sulfilimine was obtained in 65% yield.

Diphenyl(diphenylsulfilimino)sulfonium perbromied(**4c**). The compound **4c** was formed by the decomposition of **2** in benzene or AcOH, m.p. 184–4.5° from MeOH. (Found: C, 45.04; H, 3.03; N, 2.11; Calc. for $C_{24}H_{20}S_2NBr_3$: C, 46.03, H, 3.22; N, 2.24%) IR (KBr) cm^{-1} 935 (SN).

Another route to **4c**. Compound **4a** (0.1 g) was dissolved in 1 ml water, and to this was added 0.5 ml conc. HBr. The precipitated bromide salt was filtered off. The residue was dried, and dissolved in 1 ml of chloroform and Br_2 was added to this soln, chloroform was removed *in vacuo*, the residue was recrystallized from MeOH, m.p. 181–3°; IR and m.p. were the same as those from decomposition of **2**.

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