Alkyl and Aryl Sulfenimides

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Alkyl and aryl sulfenimides have been synthesized by the reaction of sulfenyl chlorides with imides in the presence of a tertiary amine. The stability of sulfenyl chloride solutions has been found to be dependent on the temperature and the polarity of the solvent. Decomposition products of cyclohexanesulfenyl chloride have been isolated and identified. Acid and base hydrolyses of cyclohexylthiophthalimide have been studied and the resulting products characterized. Mechanisms and supporting analytical data for the decomposition of cyclohexanesulfenyl chloride and the hydrolyses of cyclohexylthiophthalimide are given. Analytical methods for determination of sulfenyl chlorides and sulfenimides are reported.

N-(Trichloromethylthio)phthalimide prepared by Kittleson[2] by the reaction of trichloromethanesulfenyl chloride with sodium phthalimide is the first sulfenimide reported in literature. Klivenye and coworkers[3] reported the synthesis of several arylthiophthalimides. The desired sulfenyl chlorides were prepared by chlorination of aryl arylthiosulfates and then treated with potassium phthalimide. Other workers[4-6] synthesized several thiosuccinimides by the reactions of mono- or disulfides with N-bromosuccinimides in the presence of a catalyst such as pyridine or benzoyl peroxide. Büchel and Conte[7] also prepared several sulfenimides by the reaction of the disulfides with the desired N-bromoimides. The synthesis of N-(*o*-nitrophenylthio)-phthalimide by the reaction of the corresponding sulfenyl chloride with N-hydroxyphthalimide has been reported by Kühle.[8] Among the unsubstituted alkyl sulfenimides, only the syntheses of N-(*n*-dodecylthio)-succinimide and phthalimide have been reported.[6,7]

In this laboratory, a novel method for the synthesis of both aryl and alkyl sulfenimides has been developed. The method involves two steps. First is the preparation of sulfenyl chlorides from the corresponding thiols or disulfides. Second is the condensation of the intermediate sulfenyl chlorides with imides in the presence of a tertiary amine where R = aryl, alkyl, aralkyl and

$$\left.\begin{matrix}\mathrm{RSH}\\ \mathrm{RSSR}\end{matrix}\right\} + \mathrm{Cl} \longrightarrow \mathrm{RSCl} \qquad (1)$$

$$\mathrm{RSCl} + \mathrm{-\overset{O}{\overset{\|}{C}}NH} + \mathrm{R_3'N:} \longrightarrow \mathrm{RSN\overset{O}{\overset{\|}{C}}-} + \mathrm{R_3'\overset{H}{\overset{|}{N}}^{+}Cl^-} \qquad (2)$$

cycloalkyl and $R_3'N:$ = a tertiary amine. Tables I–V give the various types of sulfenimides prepared by this method. Their yields, melting points, and elemental analyses are also shown.

Discussion

Sulfenyl Chlorides.—Different methods for preparation of sulfenyl chlorides have been reported by several workers.[9-14] In this laboratory, sulfenyl chlorides are obtained by chlorination of thiols or disulfides in solvents such as aromatic, saturated, or chlorinated hydrocarbons.

When thiols are the starting materials, chlorination first converts them into the disulfides, which are then cleaved to give the sulfenyl chlorides. It was found

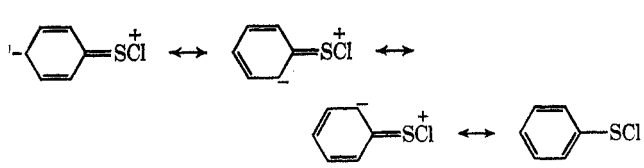
$$2\mathrm{RSH} \xrightarrow[-2\mathrm{HCl}]{+\mathrm{Cl_2}} \mathrm{RSSR} \xrightarrow{\mathrm{Cl_2}} 2\mathrm{RSCl}$$

that the first reaction is more exothermic, and nearly all of the thiol is converted into the disulfide before the second reaction is initiated.

When *t*-alkyl disulfides are used as the starting material, the cleavage usually occurs at the S–C bond rather than the S–S bond.[10]

$$\mathrm{CH_3C(CH_3)_2SSC(CH_3)_2CH_3} \xrightarrow{\mathrm{Cl_2}} \mathrm{CH_3C(CH_3)_2SSCl}$$

The aromatic sulfenyl chlorides were shown to be much more stable than the aliphatic sulfenyl chlorides. Benzenesulfenyl chloride in carbon tetrachloride did not decompose appreciably after 2 months at room temperature. In contrast, the concentration of cyclohexanesulfenyl chloride in carbon tetrachloride was reduced by one-half after 7 hr at room temperature. The higher stability of the aromatic sulfenyl chlorides may be attributed to the resonance stabilization of the benzene ring and also the absence of protons on the carbon adjacent to the sulfur atom. Aliphatic sulfenyl



chlorides with α hydrogens will react with chlorine, especially at higher temperatures, to give α-chloro-

$$\mathrm{RCH_2SCl} \xrightarrow{\mathrm{Cl_2}} \mathrm{RCH_2SCl_2} \longrightarrow \mathrm{R\overset{H}{\overset{|}{C}}SCl}\ (\mathrm{Cl})$$

(1) Department of Chemistry, Pahlavi University, Shiraz, Iran.

(2) A. R. Kittleson (to Standard Oil Development Co.), U. S. Patent 2,553,770 (1951); *Chem. Abstr.*, **45**, 6792 (1951).

(3) F. Klivenye, J. Szabo, and E. Vinkler, *Acta. Chim. Acad. Sci., Hung.*, **6**, 373 (1955); *Chem. Abstr.*, **51**, 1882 (1957).

(4) H. Miyoshi and R. Oda, *Kogyo Kagaku Zasshi*, **59**, 224 (1956).

(5) W. Groebel, *Chem. Ber.*, **92**, 2887 (1959).

(6) W. Groebel, *ibid.*, **93**, 284 (1960).

(7) K. H. Büchel and A. Conte, *ibid.*, **100**, 1248 (1967).

(8) E. Kühle and R. Wegler, *Ann.*, **616**, 183 (1958).

(9) N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946).

(10) W. A. Schulze, G. H. Short, and W. W. Crouch, *Ind. Eng. Chem.*, **42**, 916 (1950).

(11) H. Emde, German Patent 804,572 (1951); *Chem. Abstr.*, **46**, 529 (1952).

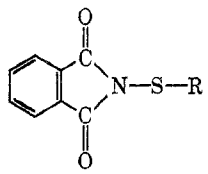
(12) I. B. Douglas, R. K. Bromer, and F. T. Martin, *J. Amer. Chem. Soc.*, **74**, 5770 (1952).

(13) C. M. Himel, U. S. Patent 2,807,615 (1957); *Chem. Abstr.*, **52**, 14706 (1958).

(14) C. G. Moore and M. Porter, *J. Chem. Soc.*, 2890 (1958).

TABLE I

SULFENIMIDES DERIVED FROM PHTHALIMIDE

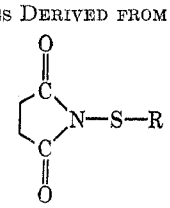


R	Registry no.	Yield, %	Mp, °C	Calcd, % N	Calcd, % S	Found, % N	Found, % S
Phenyl	14204-27-4	95	160–161	5.49	12.53	5.58	12.36
p-Chlorophenyl	14204-31-0	95	179–181	4.85	11.06	4.89	10.87
m-Tolyl	14204-29-6	94	138–139	5.16	11.9	5.18	12.14
Ethyl	17796-70-2	90	115	6.76	15.5	6.61	15.0
n-Propyl	17796-71-3	95	77–78	6.33	14.48	6.50	14.16
Isopropyl	17796-72-4	90	63.5–64	6.33	14.48	6.26	14.39
n-Butyl	17796-73-5	92	65–66	5.95	13.6	6.07	13.35
sec-Butyl	17796-74-6	90	43.5–45	5.95	13.6	6.01	13.4
t-Butyl	17796-75-7	99	130–131	5.95	13.62	6.01	13.61
Isobutyl	17796-76-8	90	69–69.5	5.95	13.62	6.19	13.62
n-Amyl	17796-77-9	90	59–60	5.61	13.26	6.02	13.3
n-Hexyl	17796-78-0	100	60	5.31	12.17	5.49	11.8
n-Octyl	17796-79-1	99	52	4.8	11.0	5.18	10.96
n-Dodecyl	14204-33-2	87	64.0–64.5	4.0	9.22	3.83	9.16
Cyclopentyl	17796-81-5	95	93–95	5.61	12.86	5.74	12.89
Cyclohexyl	17796-82-6	94	93–94	5.36	12.26	5.48	12.14
Cycloheptyl	17796-83-7	86	97–99	4.84	11.07	4.84	10.65
Isobornyl	17796-84-8	90	111–112	4.44	10.16	4.25	9.89
Benzyl	14204-26-3	81	167–167.5	5.22	11.90	5.87	11.58
α-Chlorocyclohexyl[a]	17796-86-0	89	121–122				

[a] *Anal.* Calcd for Cl: 11.89. Found: 12.12.

TABLE II

SULFENIMIDES DERIVED FROM SUCCINIMIDE



R	Registry no.	Yield, %	Mp, °C	Calcd, % N	Calcd, % S	Found, % N	Found, % S
Phenyl	14204-24-1	75	115–116	6.75	15.5	6.69	15.30
m-Tolyl	17796-88-2	80	100–102	6.33	14.48	6.51	14.31
o-Nitrophenyl	17796-90-6	85	209	11.1	12.70	10.78	13.33
p-Nitrophenyl	17796-89-3	84	173–175	11.1	12.70	10.58	12.30
Cyclohexyl	17796-91-7	87	99	6.56	15.03	6.91	15.04

sulfenyl chlorides.[12,15,16] In the case of aromatic sulfenyl chlorides, excess chlorination will cause the formation of $ArSCl_3$ without further decomposition to other by-products. The stability of the aliphatic sulfenyl chlorides in different solvents was found to be influenced by the polarity of the solvents. The stability of cyclohexanesulfenyl chloride in various solvents decreased in the following order: *n*-pentane, xylene, carbon tetrachloride, chlorobenzene, and methylene chloride. These findings indicate that the sulfenyl chloride is more stable in the less polar solvents. Figure 1 shows the change in the concentration of the cyclohexane sulfenyl chloride at room temperature with time. It shows that the decomposition of the sulfenyl chloride is much faster in carbon tetrachloride and xylene than in *n*-heptane. The half-life of the sulfenyl chloride in these solvents was 7.5, 12, and 65 hr, respectively. Figures 2 and 3 show that the decomposition of cyclohexanesulfenyl chloride is first order in *n*-heptane and second order in xylene and car-

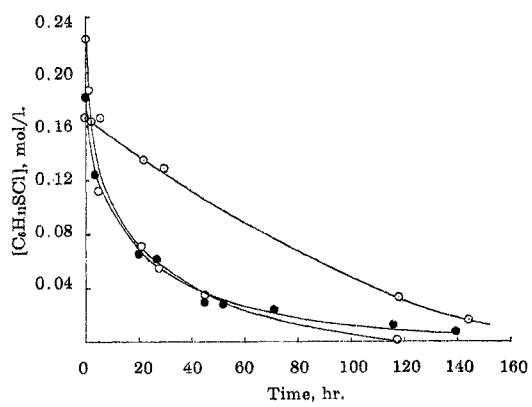


Figure 1.—Decomposition of cyclohexanesulfenyl chloride at room temperature: ⊙, in *n*-heptane; ○, in CCl_4; ●, in xylene.

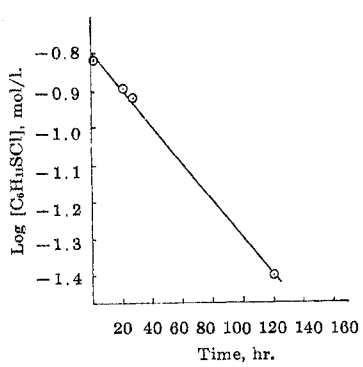
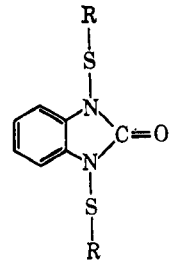


Figure 2.—Decomposition of cyclohexanesulfenyl chloride in *n*-heptane at room temperature.

(15) K. R. Bromer and I. B. Douglas, *J. Amer. Chem. Soc.*, **73**, 5787 (1951).

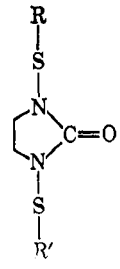
(16) R. B. Flay (California Research Corp.), U. S. Patent 3,144,482 (1964); *Chem. Abstr.*, **61**, 9404c (1964).

TABLE III
SULFENIMIDES DERIVED FROM 2-BENZIMIDAZOLINONE



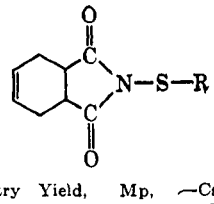
R	Registry no.	Yield, %	Mp, °C	Calcd, % N	Calcd, % S	Found, % N	Found, % S
Phenyl	17796-92-8	60	115–117	7.98	18.39	7.76	17.77
m-Tolyl	17796-93-9	70	110–110.5	7.1	16.26	7.28	16.96
o-Nitrophenyl	17796-94-0	60	270 dec	12.72	14.55	12.22	14.49
Cyclohexyl	17796-95-1	80	80–81	7.72	17.68	7.28	17.58

TABLE IV
SULFENIMIDES DERIVED FROM 2-IMIDAZOLIDONE



R	R′	Registry no.	Yield, %	Mp, °C	Calcd, % N	Calcd, % S	Found, % N	Found, % S
Phenyl	Phenyl	17796-96-2	75	77–78	9.30	21.2	8.96	21.12
p-Chlorophenyl	*p*-Chlorophenyl	17796-97-3	70	146–147	7.55	17.2	7.43	17.09
Cyclohexyl	Cyclohexyl	17796-98-4	75	80–81	8.8	20.38	9.28	20.11
Cyclohexyl	Hydrogen	17796-99-5	75	127–128	14.0	16.0	14.24	15.97

TABLE V
SULFENIMIDES DERIVED FROM TETRAHYDROPHTHALIMIDE



R	Registry no.	Yield, %	Mp, °C	Calcd, % N	Calcd, % S	Found, % N	Found, % S
Phenyl	17797-00-1	95	121–122.5	5.36	12.36	5.41	11.78
p-Chlorophenyl	17797-01-2	95	147–148	4.77	10.90	4.77	10.80
Cyclohexyl	17797-02-3	98	90–91.5	5.23	12.08	5.28	12.03

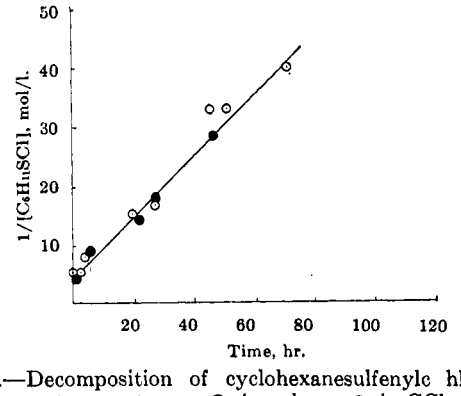
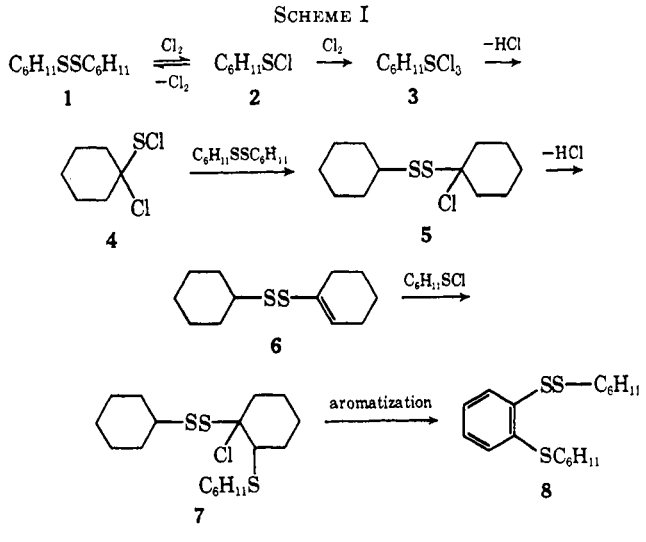


Figure 3.—Decomposition of cyclohexanesulfenylc hloride at room temperature: ⊙, in xylene; ●, in CCl_4.

bon tetrachloride. The stability of the sulfenyl chloride is also dependent on temperature as shown in Figure 4.

The major decomposition products of cyclohexanesulfenyl chloride were found to be cyclohexyl disulfide and hydrogen chloride. The pattern of formation of these products in various solvents are shown in Figures 5 and 6. A suggested mechanism for the decomposition of the sulfenyl chloride is given in Scheme I.

SCHEME I



Aromatic compound **8** was isolated as a minor product and identified by ir, nmr, mass spectroscopy, and elemental analysis. Trichloride **3** was usually observed as a yellow precipitate at low temperatures in the over-

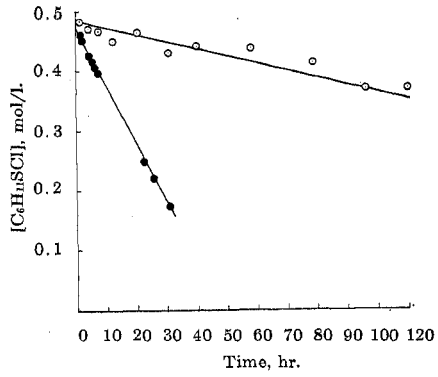


Figure 4.—Stability of cyclohexanesulfenyl chloride in Varsol no. 2 (a mixture of aromatic, olefinic, and aliphatic hydrocarbons in 28, 2, and 70%, respectively, bp 157–201°): ⊙, at 0°; ●, at room temperature (25°).

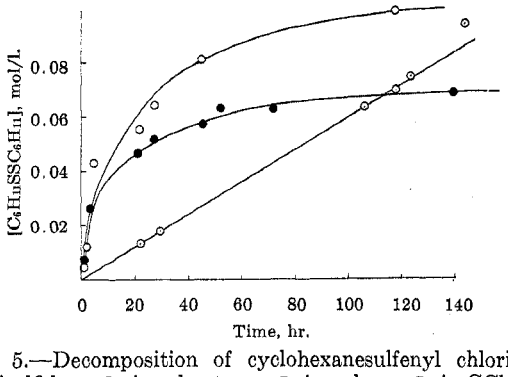


Figure 5.—Decomposition of cyclohexanesulfenyl chloride to disulfide: ⊙, in *n*-heptane; ●, in xylene; ○, in CCl_4.

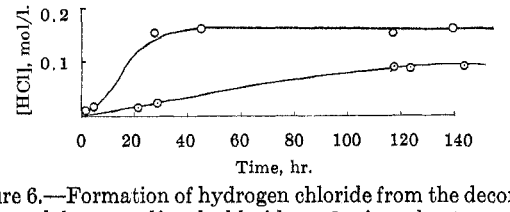
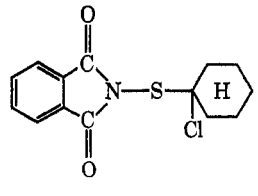


Figure 6.—Formation of hydrogen chloride from the decomposition of cyclohexanesulfenyl chloride: ⊙, in *n*-heptane; ○, in xylene and CCl_4.

chlorinated solutions of thiols. α-Chlorosulfenyl chloride **4** was prepared by chlorination of cyclohexanesulfenyl chloride. Its condensation with phthalimide gave the expected α-chlorocyclohexylthiophthalimide.



The structure of this compound was proven by ir, nmr, and elemental analysis.

Aromatic sulfenyl chlorides can be made at room temperature and practically in all solvents. However, aliphatic sulfenyl chlorides should be prepared in nonpolar media at low temperatures with no overchlorination. The chlorine addition is stopped when the assay method (see Experimental Section) shows nearly complete conversion of the thiol into the sulfenyl chloride. The preferred solvents for aliphatic sulfenyl chlorides are saturated hydrocarbons while for aromatic sulfenyl chlorides either carbon tetrachloride or saturated hydrocarbons can be used.

Sulfenimides.—The condensation step involves the reaction of the sulfenyl chloride with imides in the presence of a tertiary amine as an acid scavenger.

$$RSCl + -\overset{\overset{O}{\|}}{C}NH + R_3'N: \longrightarrow -\overset{\overset{O}{\|}}{C}NSR + R_3'\overset{\overset{H}{|}}{N}{}^{+}Cl^{-}$$

This reaction is fast and exothermic. It was found that the best yields are obtained when a polar solvent such as dimethylformamide is used. In less polar solvents the reaction is slow, and therefore the sulfenyl chloride must be added slowly and the reaction mixture heated for a certain length of time. The purity of the final product can be determined either by iodometric titration or by titration with 2-mercaptobenzothiazole (see Experimental Section).

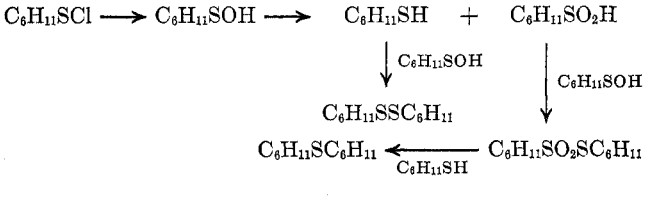
Reaction with Acids and Bases.—In order to understand the behavior of sulfenimides toward acids and bases, cyclohexylthiophthalimide was treated with triethylamine, potassium hydroxide, and hydrochloric acid. It was found that cyclohexylthiophthalimide is slightly hydrolyzed by a weak base such as triethylamine. Cyclohexylthiophthalimide, when treated with potassium hydroxide, was hydrolyzed rapidly at room temperature. One such hydrolysis gave the following products: potassium phthalate, cyclohexyl disulfide, potassium cyclohexylsulfinate, and potassium cyclohexyl sulfonate in yields of 83, 69, 17.5, and 5%, respectively. Ammonia gas was also one of the products.

The hydrolysis of cyclohexylthiophthalimide by hydrochloric acid is slower than that with potassium hydroxide. In contrast, benzothiazolesulfenamides are more susceptible to decomposition by acids rather than bases.[17] Complete hydrolysis of cyclohexylthiophthalimide was obtained under acidic conditions after 7.5 hr of refluxing at 78° in ethyl alcohol. The products obtained were phthalimide, cyclohexyl disulfide, cyclohexyl disulfide S,S-dioxide, cyclohexyl sulfide, and ethyl phthalate in yields of 92, 36, 36, 11, and 3.6%, respectively. Some ammonia gas was also detected in this reaction.

The attack of hydrogen chloride on the S–N bond of the sulfenimide produces the free imide and the sulfenyl chloride. Part of the imide is converted into diethyl phthalate and ammonia.

The sulfur products are obtained from the sulfenyl chloride probably *via* Scheme II.

SCHEME II



Experimental Section

A. Synthesis of Sulfenimides.—The general method for the preparation of these compounds involves the preparation of sulfenyl chlorides by chlorination of thiol or disulfides and

(17) Unpublished work.

subsequent condensation with the imides. Saturated hydrocarbons, carbon tetrachloride, xylene, and dimethylformamide were used as solvents. Triethylamine was used as the hydrogen chloride scavenger in the condensation step. When dimethylformamide was used as the condensation solvent, the product was precipitated by dilution with water. When other solvents were used, the solvent was evaporated, and the product precipitated by a hydrocarbon solvent such as *n*-heptane.

1. **N-(*n*-Hexylthio)phthalimide.**—Chlorine gas (14.5 g, 0.2 mol) was added to a stirred solution of 1-hexanethiol (23.6 g, 0.2 mol) in 150 ml of *n*-heptane at 0°. An assay of the resulting orange solution showed nearly complete conversion of the thiol into the sulfenyl chloride. The sulfenyl chloride solution was added dropwise to a stirred solution of phthalimide (29.4 g, 0.2 mol) and triethylamine (27.0 g, 0.27 mol) in 120 ml of dimethylformamide. After stirring for 30 min the reaction mixture was transferred to a larger beaker, and 1.5 l. of cold water was added with stirring. Upon filtering and drying a quantitative yield of colorless sulfenimide was obtained. This material was crystallized from *n*-heptane, mp 60°, 98% pure.

2. **N-(Cyclohexylthio)phthalimide.**—Chlorine gas was added to stirred solution of cyclohexanethiol (11.6 g, 0.1 mol) in 100 ml of dry carbon tetrachloride at 0° until an assay of the resulting orange solution showed quantitative conversion of the thiol into the sulfenyl chloride. The amount of chlorine needed was 9.2 g (0.13 mol). This solution was added dropwise to a stirred slurry of phthalimide (14.7 g, 0.1 mol) and triethylamine (15 g, 0.15 mol) in 200 ml of carbon tetrachloride over a period of 1 hr. After 2 hr of stirring, 250 ml of cold water was added; the carbon tetrachloride layer was separated, dried (Na_2SO_4), and evaporated under reduced pressure until approximately 150 ml of solution remained. *n*-Heptane, 500 ml, was added to the solution at 0° to precipitate a colorless sulfenimide (24.5 g, 94% yield). This material was crystallized from *n*-heptane to give a white crystalline material, mp 93–94°, 99% pure.

3. **N-(Phenylthio)phthalimide.**—Chlorine gas was added to a stirred solution of benzenethiol (55 g, 0.5 mol) in 300 ml of *n*-pentane at 0° until an assay of the resulting red orange solution showed almost quantitative conversion of the thiol into the sulfenyl chloride. The amount of chlorine needed was 39 g (0.6 mol). The sulfenyl chloride solution was added dropwise to a stirred solution of phthalimide (73.5 g, 0.5 mol) and triethylamine (60 g, 0.6 mol) in 200 ml of dimethylformamide. The reaction mixture was stirred for 30 min, transferred to a large beaker; and then 2 l. of cold water was added to give 121 g (95%) of colorless sulfenimide. This material was crystallized from ethanol, mp 160–161°, 98% pure.

B. Reaction of N-(Cyclohexylthio)phthalimide with Acids and Bases. 1. Reaction with Triethylamine.—N-(Cyclohexylthio)-phthalimide (10.4 g, 0.04 mol, 98% pure) in 100 ml of xylene was stirred and refluxed with triethylamine (4.0 g, 0.04 mol) in 10 ml of water for 5 hr. Samples of the reaction mixture were injected through glpc and showed some decomposition of the product to disulfide and phthalimide. The amount of cyclohexylthiophthalimide isolated from this mixture was 75% of the original (93% pure).

2. **Reaction with Potassium Hydroxide.**—N-(Cyclohexylthio)phthalimide (26.0 g, 0.1 mol) in 200 ml of ethanol was stirred and refluxed for 2 hr with potassium hydroxide (14.0 g, 0.25 mol) in 5.0 g of water. Upon cooling, the reaction mixture gave 20 g (83%) of potassium phthalate. The filtrate was diluted with water and extracted with ether. The ether layer was dried (Na_2SO_4) and evaporated to give 8.0 g (34%) of cyclohexyl disulfide. The aqueous layer was analyzed for cyclohexylsulfinic and cyclohexylsulfonic acids. It contained 2.6 g (17.5%) of cyclohexylsulfinic and 0.91 g (5%) of cyclohexylsulfonic acid.

3. **Reaction with Hydrochloric Acid.**—Concentrated hydrochloric acid (30 ml) was added to a solution of N-(cyclohexylthio)phthalimide (26.0 g, 0.1 mol) in 200 ml of ethanol. The mixture was refluxed with stirring for 7.5 hr. Upon cooling 13.5 g (19.8%) of phthalimide was obtained. The filtrate was diluted with water, neutralized by sodium hydroxide, and then extracted with ether. The ethereal solution was dried (Na_2SO_4) and evaporated to give 10 g of a liquid. Glpc of the liquid showed it to contain four components. Samples of these four components were collected by glpc and identified by elemental analyses and infrared spectroscopy as diethyl phthalate, cyclohexyl monosulfide, cyclohexyl disulfide, and cyclohexyl disulfide S,S-dioxide in yields of 4, 12, 42, and 42%, respectively.

C. Synthesis of N-(1-Chlorocyclohexylthio)phthalimide.—Chlorine gas (16.0 g, 0.225 mol) was added to a stirred solution of cyclohexanethiol (11.6 g, 0.1 mol) in 80 ml of carbon tetrachloride at 0°. The resulting yellow-brown α-chlorosulfenyl chloride solution was added dropwise to a solution of phthalimide (14.7 g, 0.1 mol) and triethylamine (13.7 g, 0.137 mol) in 150 ml of carbon tetrachloride. The reaction mixture was heated at 40–45° for 1 hr and transferred to a separatory funnel; 750 ml of 60° water was added to give a white crystalline sulfenimide. The carbon tetrachloride layer was separated, dried (Na_2SO_4), and evaporated to give some more of the above product (total yield 89%). Recrystallization of this product from ethanol gave a white crystalline material, mp 121–122°.

D. Assay Methods. 1. Sulfenyl Chlorides. a. The Glpc Method.—The glpc method is the preferred assay method for the sulfenyl chlorides. A known amount of sulfenyl chloride is added to a solution containing an excess amount of morpholine and a known concentration of an internal standard (dibenzyl ether or diphenyl sulfide) in benzene. The mixture is occasionally swirled for 5 min and then diluted with water. The benzene layer is injected through a silicone rubber glpc column, and the concentration of the sulfenimide and consequently that of the sulfenyl chloride solution are obtained. The amount of unreacted disulfide can also be obtained. For more accurate analysis the response factors of sulfenimide and disulfide in relation to the internal standard should be measured on a known sample previous to the analysis.

b. The Iodometric Method.—This method was developed by Kharasch and Wald[18] and is based on the oxidation of iodide ion by the sulfenyl chloride and a subsequent titration of the free iodine by thiosulfate. The limitation of this method is that other oxidizing agents will interfere with the results.

2. Sulfenimides. a. Potentiometric Titration by 2-Mercaptobenzothiazole (MBT).—This method is based on the reaction of 2-mercaptobenzothiazole with the sulfenimide to give the unsymmetrical disulfide and the free imide. The product (1 mequiv) is added to 25 ml of 0.05 *N* MBT in *t*-butyl alcohol. The solution is allowed to stand for 15 min at 50°, after which 100 ml of acetone is added and the remaining MBT is titrated with 0.07 *N* tetrabutylammonium hydroxide. The MBT potentiometric break occurs at an apparent pH 7. If there is a free acid present in the sample its potentiometric break will occur earlier, and the volume of titrant used for its neutralization must be subtracted from the total volume of the titrant. The volume of MBT solution used in the reaction is calculated, and the amount of sulfenimide can then be determined.

b. Iodometric Titration.—This method was developed by Groebel[5] and is based on the oxidation of iodide ion by sulfenimides followed by a thiosulfate titration of the free iodine. The limitation of this method is that other oxidizing agents will interfere with the results.

Registry No.—Cyclohexanesulfenyl chloride, 17797-03-4; cyclohexane disulfide, 2550-40-5.

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(18) N. Kharasch and M. M. Wald, *Anal. Chem.*, **27**, 996 (1955).