THIOCARBAMYLSULFENAMIDES[1]
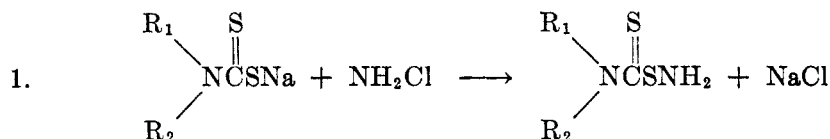
GEORGE E. P. SMITH, Jr., GLEN ALLIGER, EDWARD L. CARR, and KENNETH C. YOUNG
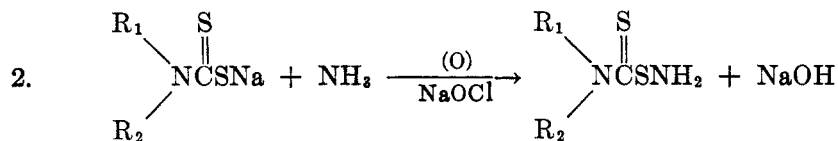
Certain thiazole-2-thiols, dithiocarbamates, and their related compounds are important accelerators for the sulfur vulcanization of rubber and rubber-like polymers. Experimental work on the preparation of thiocarbamylsulfenamides was undertaken as a natural extension of earlier studies of the corresponding thiazole derivatives (1, 2).

Unsubstituted N,N-dialkylthiocarbamylsulfenamides have been prepared by the reaction of monochloroamine and sodium N,N-dialkyldithiocarbamates (3).

$$1. \quad \underset{R_2}{\overset{R_1}{>}}N\overset{\overset{S}{\|}}{C}SNa + NH_2Cl \longrightarrow \underset{R_2}{\overset{R_1}{>}}N\overset{\overset{S}{\|}}{C}SNH_2 + NaCl$$
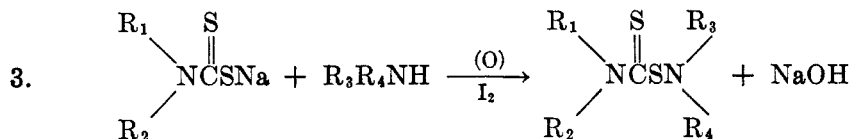
Independently of the work described in the above patents, it was found by us that these compounds may be prepared by addition of sodium dithiocarbamates and a 10% solution of sodium hypochlorite at approximately equimolecular rates to an excess of concentrated ammonia. It is possible that monochloroamine is formed as an intermediate in this reaction.

$$2. \quad \underset{R_2}{\overset{R_1}{>}}N\overset{\overset{S}{\|}}{C}SNa + NH_3 \xrightarrow[\text{NaOCl}]{\text{(O)}} \underset{R_2}{\overset{R_1}{>}}N\overset{\overset{S}{\|}}{C}SNH_2 + NaOH$$

Several of the methods which were used for the preparation of the substituted thiazolesulfenamides (1) have been found to be applicable to the preparation of the corresponding substituted thiocarbamyl analogs (3).
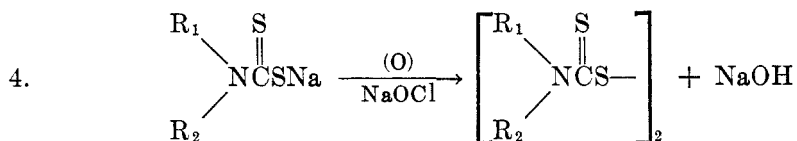
Oxidative condensation of an aliphatic amine with a N,N-dialkyldithiocarbamate in alkaline solution with iodine gave excellent yields in many cases.

$$3. \quad \underset{R_2}{\overset{R_1}{>}}N\overset{\overset{S}{\|}}{C}SNa + R_3R_4NH \xrightarrow[\text{I}_2]{\text{(O)}} \underset{R_2}{\overset{R_1}{>}}N\overset{\overset{S}{\|}}{C}S\underset{R_4}{\overset{R_3}{<}}N + NaOH$$

This equation represents the reaction previously found to be the most generally applicable to the preparation of thiazolesulfenamides (1, 2). The iodine was used in a solution of potassium iodide. Sodium hypochlorite could be used instead of
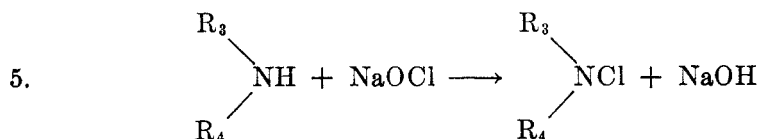
iodine, but with this oxidizing agent the product contained an appreciable amount of tetraalkylthiuram disulfide in addition to the desired sulfenamide.

4.
$$\begin{array}{c} R_1 \\ \diagdown \\ \diagup \\ R_2 \end{array} N\overset{\overset{\textstyle S}{\|}}{C}SNa \xrightarrow[\text{NaOCl}]{(O)} \left[\begin{array}{c} R_1 \\ \diagdown \\ \diagup \\ R_2 \end{array} N\overset{\overset{\textstyle S}{\|}}{C}S-\right]_2 + NaOH$$
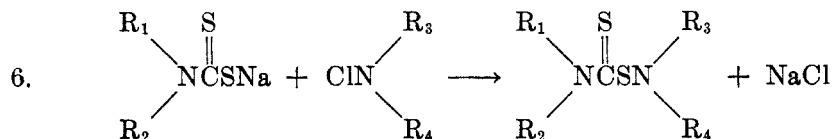
In the previous work the formation of thiazolyl disulfides was also found to be a side reaction in the preparation of the thiazole sulfenamides when either sodium hypochlorite or chlorine was used as an oxidizing agent, but this could be minimized or prevented entirely by the use of excess amine and the maintenance of the pH between 12.0 and 13.0 (1, 4). Such was not the case for the thiocarbamyl compounds. Using chlorine or sodium hypochlorite, thiuram disulfides were formed as impurities in the sulfenamide product at any pH from 10–13 and in spite of large excesses of amine.

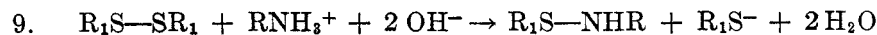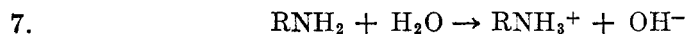Sodium hypochlorite could be successfully used, however, if the N-monochloroamine were first prepared (1, 5),

5.
$$\begin{array}{c} R_3 \\ \diagdown \\ \diagup \\ R_4 \end{array} NH + NaOCl \longrightarrow \begin{array}{c} R_3 \\ \diagdown \\ \diagup \\ R_4 \end{array} NCl + NaOH$$

and then allowed to react with a sodium N,N-dialkyldithiocarbamate (1, 3, 6).

6.
$$\begin{array}{c} R_1 \\ \diagdown \\ \diagup \\ R_2 \end{array} N\overset{\overset{\textstyle S}{\|}}{C}SNa + ClN\begin{array}{c} R_3 \\ \diagup \\ \diagdown \\ R_4 \end{array} \longrightarrow \begin{array}{c} R_1 \\ \diagdown \\ \diagup \\ R_2 \end{array} N\overset{\overset{\textstyle S}{\|}}{C}SN\begin{array}{c} R_3 \\ \diagup \\ \diagdown \\ R_4 \end{array} + NaCl$$

In several cases excellent yields were obtained by this method. Furthermore, it was possible to adjust conditions so that little or no thiuram disulfide was formed as an impurity in the product.

For the preparation of N,N-diethylthiocarbamyl-N'-cyclohexylsulfenamide a variation of the above process which involved simultaneous addition of sodium N,N-diethyldithiocarbamate and sodium hypochlorite solutions proved successful, provided that a slight excess of hypochlorite was maintained in the reaction mixture during the addition. It is probable that, under these conditions, N-monochlorocyclohexylamine was formed as an intermediate.

With regard to the probable steps involved in the reaction it has been postulated in a previous communication from this laboratory (1) that, when an oxidizing agent is added to a mixture of an amine and a metal mercaptide, the formation of the sulfenamide may be represented as follows:

7. $RNH_2 + H_2O \rightarrow RNH_3^+ + OH^-$

8. $2\,R_1S^- + (O) + H_2O \rightarrow R_1S{-}SR_1 + 2\,OH^-$

9. $R_1S{-}SR_1 + RNH_3^+ + 2\,OH^- \rightarrow R_1S{-}NHR + R_1S^- + 2\,H_2O$

Evidence that supports this proposal in preference to the assumption that a N-chloroamine is an intermediate is as follows:

1. In the presence of amines and oxidizing agents, disulfides may be converted to sulfenamides.

2. Oxidizing agents other than halogens and hypohalites can be used to oxidize mixtures of amines and metal mercaptides to sulfenamides (2).

3. In the case of thiazole sulfenamides careful adjustment of pH together with the use of excess amine was necessary to prevent the occurrence of thiazolyl disulfides in the final product (1, 4).

During the work with thiocarbamylsulfenamides a number of confirmatory observations were made.

1. Sodium hypochloride was suitably used for the preparation of thiocarbamylsulfenamides only by preparing the N-monochloroamine as an intermediate.

2. The conditions found optimum for the preparation of thiocarbamylsulfenamides *via* the N-monochloroamines were quite different from those necessary when using direct oxidative condensation of a metal mercaptide and an amine by iodine.

3. In the case of N,N-diethylthiocarbamyl-N'-cyclohexylsulfenamide, in order to obtain a good yield free from tetraethylthiuram disulfide, it was necessary to use a temperature above 25° and a 2.5-mole excess of cyclohexylamine in the direct oxidative condensation process. Indeed, when the reaction was run at a lower temperature (5–20°) the product formed contained an appreciable amount of disulfide, but merely heating the reaction mixture completed the conversion to the sulfenamide. On the other hand, when N-monochlorocyclohexylamine was used as an intermediate, there was no evidence of disufide formation at any reaction temperature from 0 to 40°, although a much better yield was obtained at lower temperatures.

In the joint oxidative condensation reaction when iodine was used as the oxidizing agent, it was necessary to use as much as 50% excess if temperatures above 25° were used. This was probably due to loss of iodine in the formation of iodate. In general, temperatures in the range of 25–50° were found suitable. Four to five moles of amine per mole of dithiocarbamate were necessary for good yields in most cases, although as little as 2.5 moles were used in a few instances.

In the chloroamine process, the N-monochloroamines were prepared by addition of sodium hypochlorite (2.5 M) to the primary amines at temperatures of 10° or below. As previously demonstrated by Coleman (5) it was necessary to maintain a 10–15% excess of amine in order to prevent the formation of dichloroamines. Those of low molecular weight were slightly soluble whereas those having five or more carbon atoms were relatively insoluble in the aqueous reaction mixtures.

In most cases the sodium N,N-dialkyldithiocarbamate was added to the suspension as prepared above without separation of the chloroamine. The sulfenamide products were then obtained as water-insoluble liquids or crystalline solids. However, as an alternative method, the chloroamine could be extracted with ether, and the reaction carried out by addition of the alkali dithiocarbamate,

TABLE I

THIOCARBAMYLSULFENAMIDES

SULFENAMIDE	YIELD, %	PREP. METHOD[a]	MOLE RATIO AMINE TO DITHIOCARBAMATE	TEMP. REACTION, °C.	M.P., °C.	ANALYSIS			
						S		N	
						Calc'd	Found	Calc'd	Found
N,N-Dimethylthiocarbamylsulfenamide									
1. Unsubstituted	73.5	II	45:1	0-10	69-71	—	—	—	—
2. N'-Ethyl	—	I	5:1	25-30	35-37	—	—	—	—
3. N'-Cyclohexyl	—	I	5:1	25-30	23-24	—	—	12.8	12.6
4. N'-Pentamethylene	80	I	4:1	50-30	77-79	31.30	31.38	—	—
N,N-Diethylthiocarbamylsulfenamide									
5. N',N'-Diethyl	77.6	I	5:1	40-25	Liquid	29.1	29.90	—	—
6. N'-Cyclohexyl	55 (80)	I (III)	2.5:1 (1.25/1)	25 (0-5)	64-65	26.00	26.20	11.40	11.35
N,N-Diallylthiocarbamylsulfenamide									
7. N'-n-Butyl	53	III	1.25:1	0-10	Liquid	—	—	11.5	11.0
N,N-Dimethallylthiocarbamylsulfenamide									
8. N'-n-Butyl	32	III	1.25:1	0-10	Liquid	—	—	10.3	10.0
N-Phenyl-N-Methylthiocarbamylsulfenamide									
9. N-Isopropyl	—	IV	1:1	30-40	72-73	26.6	26.0	11.6	11.5
10. N-Pentamethylene	—	IV	1:1	30-40	82-83	24.0	23.8	10.5	10.3
N-Tetramethylenethiocarbamylsulfenamide									
11. N'-n-Butyl	71	I	5:1	25-30	Liquid	—	—	12.8	12.9
12. N'-Pentamethylene	70	I	5:1	25-30	103-103.5	—	—	12.1	12.3
13. N'-Benzyl	57	I	5:1	25-30	93-94	25.4	25.7	11.1	10.8

	Yield	Method	Ratio	Temp.	M.p.				
N-Pentamethylenethiocarbamylsulfenamide......									
14. Unsubstituted............	—	II	30:1	0–10	54–56	—	—	—	—
15. N'-Isopropyl............	42 (45)	I (III)	5:1 (2/1)	40–30 (0–5)	52–53	29.36	29.51	12.83	13.10
16. N'-(1,3-Dimethylbutyl)......	—	I	4:1	30–25	25–27	26.00	26.37	—	—
17. N'-Cyclohexyl............	2.6 (75)	I (III)	3:1 (1.25/1)	4–10	75–75.5	24.81	24.82	10.84	10.95
18. N'-Pentamethylene......	92 (38)	I (III)	3:1 (1.25/1)	40–35	100–102	26.02	26.04	11.36	11.25
N-Oxadiethylenethiocarbamylsulfenamide (from Morpholine)									
19. N'-Isopropyl......	31	I	5:1	25	80–81	—	—	—	—
20. N'-Cyclohexyl......	50	I	3:1	15	85–86	—	—	—	—

ᵃ I. Iodine oxidation of an amine-alkali dithiocarbamate mixture.
II. Simultaneous addition of sodium hypochlorite and an alkali dithiocarbamate to the aqueous amine solution.
III. Addition of a solution of an alkali dithiocarbamate to an aqueous suspension of the N-monochloroamine.
IV. Reaction of solid alkali dithiocarbamate with an ether solution of the monochloroamine.

either as the dry salt or in aqueous solution, to the ether solution of the chloro-amine. In this case the sulfenamide was in the ether phase at the end of the reaction.

The reaction of hypochlorites with primary amines to form N-monochloro primary amines is easily reversed. For instance Coleman (5) found that shaking an ether solution of a N-monochloro primary amine with aqueous acid solutions regenerated the amine. Chapin (7) discovered that, in aqueous solution, the monochloro, dichloro, and free primary amines were in equilibrium, the relative

TABLE II (a)

SULFENAMIDES FROM N-MONOCHLOROCYCLOHEXYLAMINE AND VARIOUS MERCAPTIDES

| MERCAPTIDE	SULFENAMIDE	YIELD, %	M.P., °C.	REFERENCE, M.P., °C.
Sodium N,N-diethyldithio-carbamate	N,N-Diethylthiocarbamyl-N'-cyclohexylsulfenamide	80	64.5–65.5	(See Table I)
Sodium benzothiazole-2-mercaptide	N-Cyclohexylbenzothiazole-2-sulfenamide	86	98 –101	102
Sodium 4,5-dimethylthiazole-2-mercaptide	N-Cyclohexyl-4,5-dimethyl-thiazole-2-sulfenamide	82	93 –94	92–94

TABLE II (b)

SULFENAMIDES FROM THE SODIUM SALT OF 2-MERCAPTOBENZOTHIAZOLE AND VARIOUS CHLOROAMINES

N-MONOCHLOROAMINE	SULFENAMIDE	YIELD, %	M.P., °C.	REFERENCE, M.P., °C.
N-Monochloroisopropylamine	N-Isopropylbenzothiazole-2-sulfenamide	40	90–93	93–94
N-Monochloro-sec-butyl-amine	N-sec-Butylbenzothiazole-2-sulfenamide	70	49–49.5	49–50
N-Monochloro-(1-methyl-butyl)amine	N-(1-Methylbutyl)benzo-thiazole-2-sulfenamide	86	55–58	58–60

The references for melting points of the thiazolesulfenamides in this table are given in Ref. (1).

quantity of each depending on the pH of the solution. At pH above 8.5, pure monochloroamine was found.

If, therefore, one adds sodium hypochlorite to an excess of primary amine, the reaction may be represented as follows:

10. $RNH_2 + Cl^+ \rightleftharpoons RNHCl + H^+$
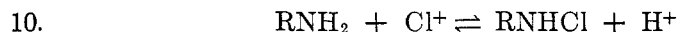
Depending on the molecular weight of the amine, one would expect the com-pleteness of chloroamine formation to depend on the pH, and on the solubility of the chloroamine. It follows that the yield of sulfenamide obtained by addition of alkali mercaptide to an aqueous suspension of N-monochloro primary amine prepared from sodium hypochlorite and amine would depend on these same factors of pH and solubility.
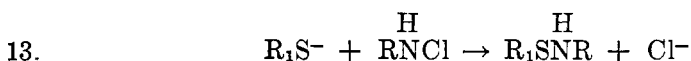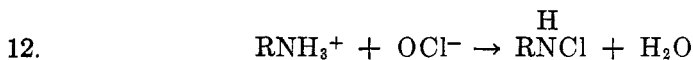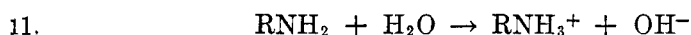
Actually it was found that the yield of sulfenamide increased

1. As the concentration of reactants was increased, *i.e.* as the amount of the aqueous phase was decreased.

2. As the temperature was decreased.

3. By saturation of the aqueous phase with salt.

4. By use of excess amine or chloroamine.

For given conditions of temperature and concentration, the yield of sulfenamide should be independent of the mercaptide used, being about the same in each case for a given N-monochloroamine and increasing as the molecular weight of the chloroamine was increased. The results summarized in Tables II (a) and II (b) support this assumption. Table II (a) gives the yields of sulfenamide which resulted from the reaction, under identical conditions, of N-monochlorocyclohexylamine with three mercaptides. Table II (b) shows the results of the reaction of sodium benzothiazole-2-mercaptide with three different N-monochloroamines, the conditions being the same for each case.

The effect of pH was difficult to determine since at a pH lower than 13.0 local over-heating from the heat of reaction initiated decomposition of the chloroamine. However, in one preparation of N,N-diethylthiocarbamyl-N'-cyclohexylsulfenamide, the pH was maintained at 12.0–12.5 by periodic additions of sulfuric acid. The yield was much lower and the product less pure than that obtained from preparations where the pH was 13.0 to 13.5. Attempts to control the pH at a value lower than 13.0 by dilution of the reaction mixture also decreased the yield. This may be ascribed to a shifting of the equilibrium of reaction 10 to the left.

The above experimental facts support the formulation of the chloramine process in the following steps as discussed in reference (1):
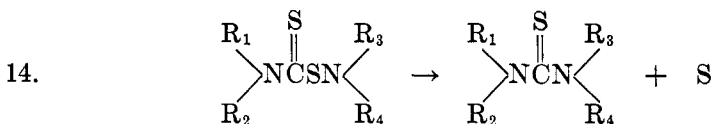
11. $$RNH_2 + H_2O \rightarrow RNH_3^+ + OH^-$$

12. $$RNH_3^+ + OCl^- \rightarrow R\overset{H}{N}Cl + H_2O$$

13. $$R_1S^- + R\overset{H}{N}Cl \rightarrow R_1S\overset{H}{N}R + Cl^-$$

The optimum conditions as determined for the chloroamine and oxidative condensation processes may be summarized as follows:

	OXIDATIVE CONDENSATION PROCESS	CHLOROAMINE PROCESS
Temperature	0–50°	−10° to +10°
pH	12.0–12.5	13
Concentration of mercaptide	*Ca.* 0.5 molar	2 to 3 molar
Amine/mercaptide ratio	1.25 to 5	1.10 to 1.25

These conditions are approximately those required for the optimum reaction of disulfide with amine in the oxidative condensation process and for the optimum formation of chloroamine in the chloroamine process.

The thiocarbamylsulfenamides are readily decomposed by heating or long

standing. The products of such decompositions were found to be thioureas formed from the sulfenamides by loss of sulfur.

14.
$$\underset{R_2}{\overset{R_1}{>}}NC\underset{}{\overset{S}{\|}}SN\underset{R_4}{\overset{R_3}{<}} \rightarrow \underset{R_2}{\overset{R_1}{>}}NC\underset{}{\overset{S}{\|}}N\underset{R_4}{\overset{R_3}{<}} + S$$

This is in contrast to the decomposition of thiazole-2-sulfenamides which usually decompose with the formation of thiazolyl disulfides.

The thiocarbamylsulfenamides are readily split by aqueous acids to give products which were not identified.

<div align="center">EXPERIMENTAL</div>

To prepare the sodium N,N-dialkyldithiocarbamates equimolecular quantities of sodium hydroxide and the secondary amine were dissolved in water and the carbon disulfide added slowly with stirring. The solution was cooled meanwhile. Yields were assumed to be theoretical. Members of the series prepared from high molecular weight (e.g., from di-2-ethyl-n-hexyl) amines formed slowly and it was necessary to heat to 60° to complete the reactions. If the dithiocarbamate separated from solution, alcohol was used to increase the solubility. The concentration was generally in the range 0.3 to 2.0 molar.

The iodine-potassium iodide solution was about 0.5 molar with respect to iodine. Water-insoluble amines such as dibutylamine were brought into solution by addition of alcohol to the reaction mixture.

N-Monochloroamines were prepared by adding a 10–15% solution of sodium hypochlorite to the amine at 10° or below. It was necessary to use a 10–15% excess of amine in preparing a N-monochloro primary amine in order to prevent the formation of any dichloroamine. The monochloroamines were separated as oils or crystalline solids. The solubility of the monochloroamines decreased as the molecular weight of the monochloroamine increased.

A number of the thiocarbamylsulfenamides prepared proved to be liquids at room temperature. The sensitivity of these compounds to acid materials and to heat eliminated extraction with aqueous acids or distillation as means of purification. However, the appearance and solubility as well as the method of preparation indicated them to be sulfenamides. These liquid materials included N,N-diethylthiocarbamylsulfenamide; the N'-isopropyl and N'-cyclohexyl derivatives of N,N-dimethylthiocarbamylsulfenamide; the N'-isopropyl, N'-(1-methylbutyl), and N'-cyclopentamethylene derivatives of N,N-diethylthiocarbamyl-sulfenamide; the N',N'-di-n-butyl and N'-cyclopentamethylene derivatives of N,N-di-n-butylthiocarbamylsulfenamide; the N'-(1-methylbutyl)-N-cyclopentamethylenethiocar-bamylsulfenamide; the N'-(1-methylpropyl), and N'-(1-methylbutyl) derivatives of N-oxadiethylenethiocarbamylsulfenamide (from morpholine). The N'-isopropyl derivatives of N,N-di-(2-ethylhexyl)thiocarbamylsulfenamide and N,N-di-n-laurylthiocarbamyl-sulfenamide were waxy materials melting at 55–60° and 150–165° respectively. They were obtained in small amounts but were not definitely characterized.

All of the crystalline thiocarbamylsulfenamides, together with methods of preparation and properties, are listed in Table I. A few typical procedures are given below.

N,N-Dimethylthiocarbamylsulfenamide. An aqueous solution of sodium N,N-dimethyl-dithiocarbamate was prepared from 4 g. (0.1 mole) of sodium hydroxide, 18 g. (0.1 mole) of an aqueous solution of dimethylamine (25%), and 7.6 g. (0.1 mole) of carbon disulfide. The solution was diluted to a volume of 75 ml. This solution and 75 ml. of a 10% sodium hypochlorite solution were added dropwise at equal rates to 300 ml. of cold conc'd aqueous ammonia. After a time a perfectly white, flocculent precipitate began to form. When the addition of dithiocarbamate and hypochlorite solution was completed, the solid material was dried and weighed; yield, 10 g. (73.5%), m.p. 69–71°, (uncorr.).

N,N-DIETHYLTHIOCARBAMYL-N'-CYCLOHEXYLSULFENAMIDE

(a) *Use of iodine as oxidizing agent.* A solution of sodium N,N-diethyldithiocarbamate was prepared from 146 g. (2.0 moles) of diethylamine, 80 g. (2.0 moles) of sodium hydroxide, and 152 g. (2.0 moles) of carbon disulfide in 800 ml. of water. To this solution was added 800 g. (8 moles) of cyclohexylamine. Next, at a temperature of 15–20°, was added slowly over a period of 1½ hours a solution of 508 g. (2.0 moles) of iodine and 500 g. of potassium iodide in 2 liters of water. After about half of the iodine solution had been added the temperature was raised to 31° and the addition completed. The reaction mixture was diluted to 8 liters and the precipitate washed and dried. Yield 395 g., (82%), m.p., 62–65°, (uncorr.).

(b) *Use of sodium hypochlorite as an oxidizing agent. First method.* In 350 ml. of an aqueous solution of 35.6 g. (0.36 moles) of cyclohexylamine and 56.4 g. (0.33 mole) of sodium, N,N-diethyldithiocarbamate were placed a Beckman "Type E" glass electrode and a calomel electrode connected to a Beckman pH meter. The pH of the solution was adjusted to 12.0 by addition of sulfuric acid solution (40%). After bringing the reaction mixture to 30°, it was maintained at that temperature while 0.39 mole of sodium hypochlorite (230 ml., 1.71 M) was added slowly, with simultaneous addition of acid to maintain the pH at 12.0–12.5.

After all of the hypochlorite solution had been added the oily solid which had separated was collected. Treatment with petroleum ether served to separate the less soluble tetraethylthiuram disulfide, 27 g. (55%), m.p. 69–71°, from the N,N-diethylthiocarbamyl-N'-cyclohexylsulfenamide, 15.7 g. (19%), m.p. 56–59°.

(c) *Use of sodium hypochlorite as an oxidizing agent. Second method.* To 37.6 g. (0.38 mole) of cyclohexylamine were added simultaneously 0.38 mole of sodium hypochlorite (216 ml., 1.78 M) and 0.33 mole of sodium N,N-diethyldithiocarbamate (192 ml., 1.7 M solution) the relative rate of addition being such that the hypochlorite added was always slightly in excess of the dithiocarbamate. Meanwhile, the temperature was maintained at 5–8° and the mixture stirred vigorously. When the addition was completed the reaction mixture was stirred for one hour. The white crystalline material which had precipitated was washed, dried, and weighed. Yield, 44.4 g. (54%); m.p. 62.5–64.5° (uncorr.).

(d) *Use of N-monochlorocyclohexylamine.* To 34.5 g. (0.35 mole) of cyclohexylamine was added 0.32 mole of sodium hypochlorite (179 ml., 1.79 M) the temperature being maintained at 5–10°. The N-monochlorocyclohexylamine separated as a pure white crystalline solid. A portion was washed five times with ice-water and dried on a porous plate in a vacuum desiccator for two hours. Analysis for positive chlorine by the thiosulfate method gave the following results:

Calc'd for $C_6H_{12}ClN$: Cl⁺, 26.53. Found: Cl⁺, 26.93.

To 0.32 mole of the monochloroamine so prepared but not separated from the reaction mixture was added slowly, and with stirring at a temperature of 5°, 0.30 mole of sodium N,N-diethyldithiocarbamate (158 ml., 1.9 M). The reaction mixture was allowed to come to room temperature overnight and the white precipitate dried. Yield, 59 g., (80%); m.p. 59–64°. After one recrystallization from petroleum ether, m.p. 64–65.5° (uncorr.).

N-Cyclopentamethylenethiocarbamyl-N'-cyclopentamethylenesulfenamide. A solution of sodium cyclopentamethylenedithiocarbamate (0.47 mole) was prepared from 40 g. of piperidine, 35.8 g. of carbon disulfide, and 18.8 g. of sodium hydroxide in water. A clear solution was obtained by diluting to a volume of 200 ml. and heating to 45–50°.

To this solution was added 3.76 moles of piperidine and then, slowly and with stirring, 119.6 g. (0.47 mole) of iodine dissolved in a solution of 120 g. of potassium iodide in one liter of water. The temperature of the reaction mixture was initially 45°. The iodine-potassium iodide solution was added at such a rate that the temperature fell slowly and was 35° when the addition had been completed. The white crystalline precipitate was washed well and dried. Yield, 105 g., (91.5%). After one recrystallization from petroleum ether, m.p. 100° (uncorr.).

N-Oxadiethylenethiocarbamyl-N'-isopropylsulfenamide. An aqueous solution of 0.227

mole of sodium N-oxadiethylenedithiocarbamate was prepared in the usual way from 19.8 g. of morpholine, 17.3 g. of carbon disulfide, 9.1 g. of sodium hydroxide, and water. This solution was then diluted to a volume of 500 ml. and 67 g. (1.13 moles) of isopropylamine was added. To the resulting solution was added slowly and with stirring an aqueous solution (400 ml.) of 57.7 g. (0.27 mole) of iodine and 58 g. of potassium iodide. The reaction proceeded smoothly at room temperature. For a short time the fine white precipitate, which formed as the iodine contacted the solution, redissolved immediately. Later a permanent crystalline precipitate began to form. This white solid was washed thoroughly and dried. Yield, 15.8 g., (31.5%); m.p. 79–80° (uncorr.).

N-sec-Butylbenzothiazole-2-sulfenamide. To 35.3 ml. (0.35 mole) of *sec*-butylamine was added with stirring 0.30 moles (166.6 ml., 1.8 *M*) of sodium hypochlorite. Meanwhile, the temperature was maintained at 0 to −5°. To the suspension of N-monochloro-*sec*-butylamine so formed was added a solution of 0.30 mole of sodium 2-benzothiazolylmercaptide in 100 ml. of water, the temperature being maintained at 0 to −5° as before. The solid which separated was dried. Yield, 49 g., (70%). Recrystallized from carbon tetrachloride, 49–49.5° (uncorr.).

Decomposition of thiocarbamylsulfenamides. A sample of N-cyclopentamethylenethiocarbamyl-N'-cyclopentamethylenesulfenamide decomposed after several months storage. The decomposition product was a brown oil. Extraction with alcohol left a residue which proved to be mainly sulfur. The soluble portion, after recrystallization, melted at 57.5–58.5°. A mixture melting point with a known sample of N,N'-dipentamethylenethiourea, m.p. 55.5–57°, melted at 55–57°, (uncorr.).

Anal. Calc'd for $C_{11}H_{20}N_2S$: S, 15.10; N, 13.18.
    Found: S, 15.29; N, 12.6.

A sample of N-cyclohexyl-N'-pentamethylenethiocarbamylsulfenamide decomposed on standing. Recrystallization of the residue first from alcohol and water and then from gasoline yielded a compound which melted at 128–130°. A mixture melting point with an authentic sample of N-cyclohexyl-N'-pentamethylenethiourea prepared from cyclohexyl isothiocyanate and piperidine, m.p. 129–131°, showed no depression.

An attempt to prepare a thiocarbamylsulfenamide by oxidative condensation of cyclohexylamine and the sodium dithiocarbamate derived from N-*n*-butyl-2-methylpiperazine produced an oil, presumably the desired sulfenamide, which decomposed after standing a day. Recrystallization of the residue from ether-petroleum ether, and then from alcohol-water yielded a material melting at 88–89°. Analysis of this compound indicated it to be N-cyclohexyl-N'-(N-*n*-butyl-2-methylpiperazyl)thiourea.

Anal. Calc'd for $C_{16}H_{31}N_3S$: N, 14.14. Found: N, 14.21.

A sample of N,N-dimethylthiocarbamyl-N'-cyclohexylsulfenamide was decomposed by heating on a hot plate at 80–100°. Recrystallization from toluene and alcohol yielded a material, m.p. 178–180°, which showed no lowering of melting point when mixed with a known sample of *N,N'-dicyclohexylthiourea.* The formation of the symmetrically substituted thiourea from the unsymmetrically substituted thiocarbamylsulfenamide indicates that an amine exchange reaction took place, with volatilization of dimethylamine and its replacement by cyclohexylamine.

SUMMARY

Methods previously used for the preparation of thiazolesulfenamides have been used in preparing the thiocarbamylsulfenamides. The use of N-monochloro primary amines as intermediates in the preparation of both thiazole- and thiocarbamyl-sulfenamides has been developed.

AKRON 17, OHIO

REFERENCES

(1) CARR, SMITH, AND ALLIGER, preceding article.

(2) (a) HARMAN, *Ind. Eng. Chem.*, **29,** 205 (1937); U. S. Patent 2,191,656 (1940); (b) ZAUCKER, U. S. Patent Reissue 19,286 (1934).

(3) (a) HANSLICK, U. S. Patent 2,318,482 (1943); U. S. Patent 2,285,813 (1942); (b) U. S. RUBBER Co., Brit. Patent 538,112 (1941); (c) SMITH AND CARR, U. S. Patents, 2,381,392 (1945), and 2,424,921 (1947); (d) COOPER, U. S. Patent 2,333,468 (1943).

(4) ASHWORTH, U. S. Patent 2,268,467 (1941).

(5) (a) MEISENHEIMER, *Ber.*, **46,** 1148 (1913); (b) BERG, *Ann. chim. et phys.*, [7], **3,** 319 (1894); (c) MARCKWALD AND WILLE, *Ber.*, **56,** 1320 (1923); (d) COLEMAN, *J. Am. Chem. Soc.*, **55,** 3001 (1933); (e) ALLIGER, U. S. Patent 2,459,759 (1949).

(6) (a) ZAUCKER, U. S. Patent Reissue 19,286 (1934); (b) I. G. FARBENINDUSTRIE, Brit. Patent 377,730 (1932); (c) HARMAN, U. S. Patent 2,171,305 (1939).

(7) (a) SOPER, *J. Chem. Soc.*, **125,** 768 (1924); (b) CHAPIN, *J. Am. Chem. Soc.*, **51,** 2112 (1929).