

G. F. G. Patterson participated in the development of the process. A significant portion of the analytical work was done by R. H. Dorris and L. R. Randles.

#### Literature Cited

- (1) Assoc. Offic. Agr. Chemists, "Official Methods of Analysis," 7th ed., pp. 10-11, 1950.
- (2) Cain, G. A., U. S. Dept. Commerce, *FIAT Final Rept.* 985 (PB 60887) (November 1946).
- (3) Harley, G. T., and Atwood, G. E., *Ind. Eng. Chem.*, 39, 43-7 (1947).
- (4) Hignett, T. P., *Chem. Eng.*, 58, 166-9 (May 1951).
- (5) Houston, E. C., Hignett, T. P., and Dunn, R. E., *Ind. Eng. Chem.*, 43, 2413-18 (1951).
- (6) Lonza Elektrizitätswerke, Brit. Patent 294,117 (July 14, 1927).
- (7) Lonza Elektrizitätswerke, French Patent 657,288 (July 11, 1928).
- (8) Lonza Elektrizitätswerke (Emil Lüscher and Samuel Ruosch), Swiss Patent 129,891 (July 14, 1927).
- (9) Lonza Elektrizitätswerke und chemische Fabrik A.-G., German Patent 502,435 (July 14, 1928).
- (10) Potasse et Engrais Chimiques, Brit. Patent 639,783 (July 5, 1950).
- (11) Striplin, M. M., Jr., McKnight, D., and Hignett, T. P., *Ind. Eng. Chem.*, 44, 236-42 (1952).
- (12) Turrentine, J. W., U. S. Patent 2,134,013 (Oct. 25, 1938).
- (13) *Ibid.*, U. S. Patent 2,211,918 (Aug. 20, 1940).

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## **N-Trichloromethylthio Compounds Evaluated as Fungicides**

# **FUNGICIDES**

## **Preparation and Some Properties of N-Trichloromethylthiotetrahydrophthalimide**

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The synthesis and properties of *N*-trichloromethylthiotetrahydrophthalimide have been studied in view of the current interest in this compound as a commercial agricultural fungicide. Also, 17 additional compounds containing the *N*-trichloromethylthio group were synthesized and evaluated for fungicidal activity. The purpose of this work was to determine whether the *N*-trichloromethyl group is the group primarily responsible for the fungicidal activity. The reaction of perchloromethyl mercaptan with sodium  $\Delta^4$ -tetrahydrophthalimide in aqueous solution is extremely rapid. The time required for completion is largely governed by the degree of dispersion of perchloromethyl mercaptan in the aqueous phase. Rapid completion of the reaction and temperature control are important variables in obtaining high yields of captan. Temperatures higher than 20° C. and long reaction times result in side reactions involving hydrolysis of the intermediates, perchloromethyl mercaptan and sodium  $\Delta^4$ -tetrahydrophthalimide. All the *N*-trichloromethylthio derivatives prepared in this work were found to be highly active fungicides, indicating that the *N*-trichloromethylthio group is the active portion of the molecule.

THE COMPOUND *N*-TRICHLOROMETHYLTHIOTETRAHYDROPHTHALIMIDE (commonly known as SR-406 or captan, the common name approved by the Interdepartmental Committee on Pest Control) is a member of a new class of highly active organic fungicides, which is cur-

rently undergoing commercial development as an agricultural pesticide. This group of compounds is characterized by the  $\text{N}(\text{SCCl}_3)$  group, and is formed by the reaction of perchloromethyl mercaptan with imides, hydantoin, 2,4-oxazolidinediones, and certain amides

and amines (7). Their early screening and agricultural development were conducted in a joint project with Rutgers University and New Jersey Agricultural Experiment Station staffs. This paper deals with captan, because its preparation and properties have been more

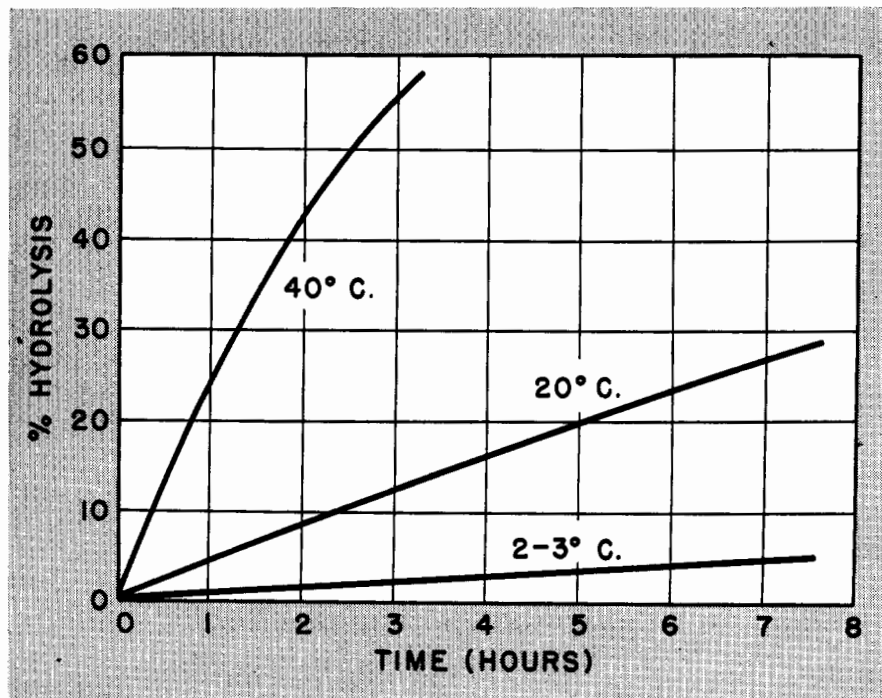
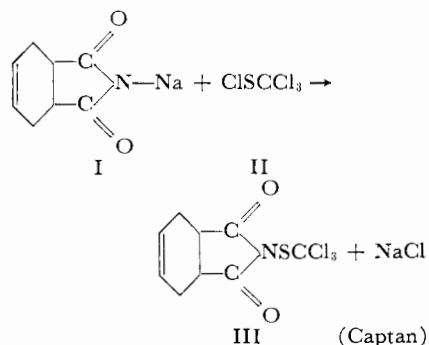


Figure 1. Hydrolysis of sodium  $\Delta^4$ -tetrahydrophthalimide in aqueous solution

fully investigated than those of the other compounds of this class.

#### Captan Synthesis

Captan (III) is synthesized by the reaction of sodium  $\Delta^4$ -tetrahydrophthalimide (I) with perchloromethyl mercaptan (II).



The reaction is carried out in aqueous solution, by adding perchloromethyl

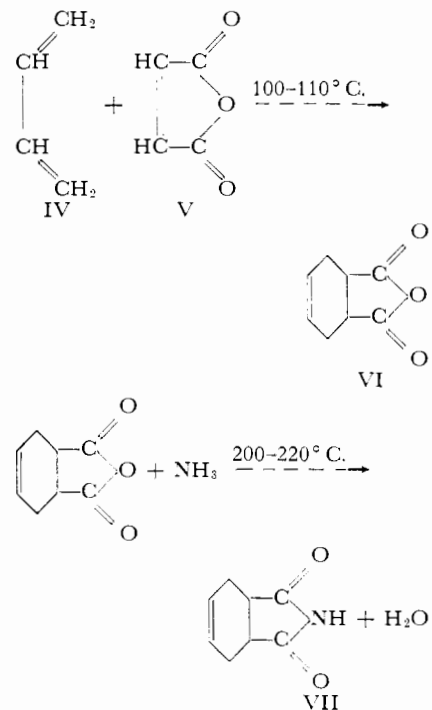
Table I. Solubility of Captan at 26° C.

Solvent	Solubility, Grams/100 ml.
Chloroform	7.78
Tetrachloroethane	8.15
Cyclohexanone	4.96
Dioxane	4.70
Benzene	2.13
Toluene	0.69
<i>n</i> -Heptane	0.04
Ethanol	0.29
Ethyl ether	0.25

mercaptan to the dissolved sodium imide (I) under good mixing conditions. Captan precipitates out as a white solid, which is then recovered by filtration (2).

The intermediate,  $\Delta^4$ -tetrahydrophthalimide (VII), is readily formed by the Diels-Alder condensation of maleic anhydride (V) with butadiene (IV). Butadiene (gas) is bubbled into molten maleic anhydride at a temperature of 100° to 110° C. until butadiene absorption becomes negligible. If good mixing of the anhydride is maintained, butadiene can be added at such a rate as

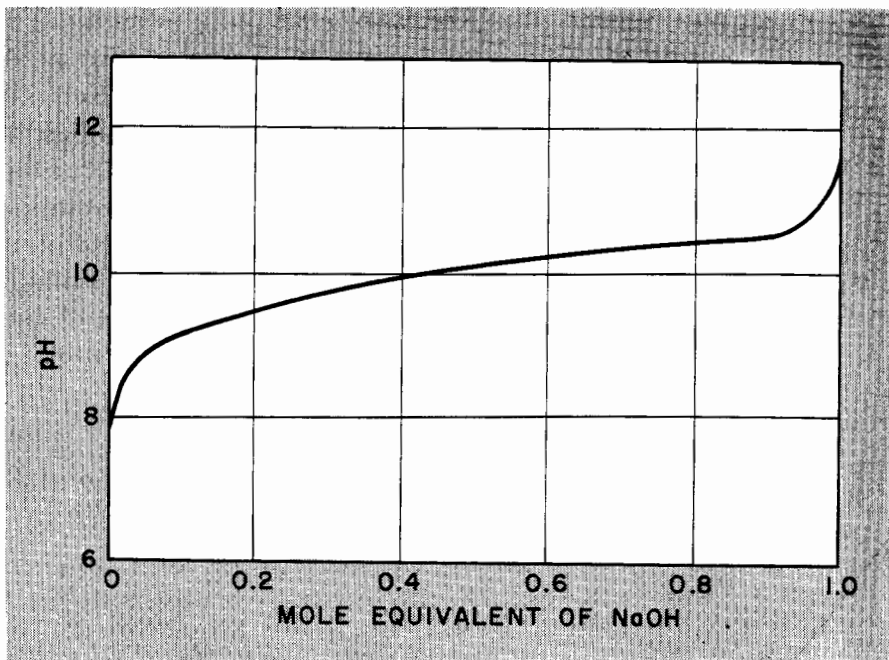
to give complete reaction within 1.5 hours. The product tetrahydrophthalic anhydride (VI) is then heated to 200° to 220° C. in a flask equipped with a stirrer, heater, condenser, and water trap. Anhydrous ammonia is added to the stirred anhydride until ammonia absorption is complete. Reaction is complete when the theoretical quantity of water is collected in the water trap.



Based on maleic anhydride, 97% yields of 95 to 97% purity tetrahydrophthalimide are obtained in this preparation.

Perchloromethyl mercaptan (II) is formed by the chlorination of carbon di-

Figure 2. Titration of  $\Delta^4$ -tetrahydrophthalimide with sodium hydroxide in aqueous solution

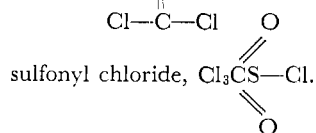


sulfide at 20° to 25° C. using iodine catalyst. It can be obtained in 75 to 80% yield by vacuum fractionation of the chlorination mixture to remove overhead carbon disulfide, sulfur dichloride, carbon tetrachloride, and sulfur monochloride and recovering 97 to 98% purity perchloromethyl mercaptan as bottoms. To minimize perchloromethyl mercaptan decomposition in the fractionation step, the still pot temperature should be maintained below 100° C. by applying suitable vacuum.

**Reaction Conditions** Two important variables other than purity of intermediates in the synthesis of captan from perchloromethyl mercaptan and  $\Delta^4$ -tetrahydrophthalimide are temperature and degree of mixing.

The temperature of reaction is of importance from the standpoint of its effect on the stability of sodium  $\Delta^4$ -tetrahydrophthalimide in aqueous solution. The rate of the sodium imide hydrolysis at several temperatures is shown in Figure 1. At temperatures below 20° C., less than 5% hydrolysis is observed in 1 hour.

Perchloromethyl mercaptan shows negligible decomposition on stirring in water at 3° to 4° C. for 3 hours, and at 25° C. less than 2 weight % decomposition is observed in the same period of time. The primary products of decomposition at these temperatures are thiophosgene,  $\text{S}=\text{C}=\text{S}$ , and trichloromethyl



In addition to temperature control, the degradation of sodium  $\Delta^4$ -tetrahydrophthalimide and perchloromethyl mercaptan can be minimized by carrying out their coupling as rapidly as possible. The formation of captan from its intermediates is extremely rapid, being similar in this respect to an acid-base reaction. Rapid completion of the reaction can be attained by efficient mixing to provide good dispersion of the insoluble perchloromethyl mercaptan in the aqueous sodium imide solution.

Complete reaction of sodium  $\Delta^4$ -tetrahydrophthalimide is determined by measuring the pH of the reaction mixture. From the curve (Figure 2) obtained by titrating  $\Delta^4$ -tetrahydrophthalimide with sodium hydroxide in aqueous solution (to form a 15% sodium imide solution), it is apparent that essentially all of sodium  $\Delta^4$ -tetrahydrophthalimide is reacted at a pH of 7 to 7.5.

**Properties of Captan** Captan is an odorless, colorless crystalline compound having a melting point of 172–173° C. and density of 1.69

grams per ml. It is only slightly soluble in many of the common organic solvents, as is shown by Table I.

This compound is stable, even in the presence of moisture, at room temperature for prolonged storage periods. Heating at 100° C. for several days results in slow decomposition; at 200° C. rapid degradation is observed. Captan is slowly decomposed by water at temperatures over 60° C., and by refluxing methanol. At 135° to 140° C., *p*-chlorophenol reacts with captan, removing 85 to 90% of the theoretical chlorine in the form of hydrochloric acid. Strong caustic solutions cause rapid decomposition at room temperature, but the compound can be recrystallized from acetic acid solutions.

In addition to the fungicidal activity, captan has been demonstrated to stimulate plant growth. This is observed in the improved growth of seedlings after seed treatment with captan, and in the rooting of cuttings from azaleas and hydrangeas. The color and finish of some varieties of apples (Golden Delicious and Stamen Winesap) are enhanced as a result of applying captan in a fungicidal spray schedule.

#### Other $\text{NSCCl}_3$ Derivatives

Other compounds containing the  $\text{NSCCl}_3$  group were prepared by the procedure described for the synthesis of

captan. These derivatives were tested for fungicidal activity in a cooperative project at Rutgers University under the supervision of R. H. Daines and Lyle E. Hagmann. The slide germination technique (3) for fungicidal testing against the fungi *Alternaria solani* and *Sclerotinia fructicola* was used in the laboratory screening of these compounds. The  $LD_{50}$  inhibiting concentrations of 18 derivatives are given in Table II.

#### Conclusions

The imide and 2,4-oxazolidinedione derivatives showed generally greater fungicidal activity against these two fungi than the hydantoin or sulfonamide compounds.

#### Literature Cited

- (1) Kittleston, A. R., *Science*, **115**, 84–6 (1952).
- (2) Kittleston, A. R., and Yowell, H. L. (to Standard Oil Development Co.), U. S. Patent 2,553,771 (May 22, 1951).
- (3) Wellman, R. H., and McCallan, S. E. A., *Contrib. Boyce Thompson Inst.*, **13**, 171 (1943).

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Table II. Fungicidal Activity of *N*-Trichloromethylthio Derivatives

Imide	$LD_{50}$ Inhibiting Concn., P.P.M.	
	<i>Alt. solani</i>	<i>Scler. fructicola</i>
Trichloromethylthio Imides		
Tetrahydrophthalimide	1–10	<1
Phthalimide	1–10	<1
3,6-Endomethylene tetrahydrophthalimide	1–10	1–10
4-Nitrophthalimide	<1	<1
Succinimide	<1	<1
<i>N</i> -Trichloromethylthio Hydantoins		
Hydantoin		
5,5-Dimethylhydantoin	10–100	1–10
1-Nitro-5,5-dimethylhydantoin	1–10	1–10
1-Acetyl-5,5-dimethylhydantoin	1–10	1–10
5-Methyl-5-isobutylhydantoin	10–100	1–10
<i>N</i> -Trichloromethylthio 2,4-Oxazolidinediones		
2,4-Oxazolidinedione		
5,5-Dimethyl-2,4-oxazolidinedione	<1	<1
5-Methyl-5-ethyl-2,4-oxazolidinedione	<1	<1
5-Methyl-5-cyclopropyl-2,4-oxazolidinedione	1–10	1–10
5-Methyl-5-isobutyl-2,4-oxazolidinedione	<1	<1
5,5-Pentamethylene-2,4-oxazolidinedione	<1	<1
5-Methyl-5-phenyl-2,4-oxazolidinedione	1–10	1–10
<i>N</i> -Trichloromethylthio Sulfonamides and Imides		
Sulfonamide or Imide		
<i>N</i> -Butyl benzene sulfonamide	10–100	10–100
<i>N</i> -Phenyl benzene sulfonamide	10–100	10–100
<i>o</i> -Benzoic sulfimide	1–10	1–10