

Synthesis and Herbicidal Activities of Some New Compounds

Generating 2,6-Dichlorobenzonitrile

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2,6-Dichlorothiobenzamide (I) was condensed with aldehydes. Condensation in neutral solutions with formaldehyde or chloral yielded products with the moiety $-\text{C}(=\text{S})\text{NHCH}(\text{OH})-$. Under acid conditions condensation of two molecules of I with the carbonyl function of aliphatic aldehydes as well as with aromatic aldehydes gave compounds with the moieties $-\text{C}(=\text{S})\text{NHCH}(-)\text{SC}(=\text{NH})-$ and

$-\text{C}(=\text{S})\text{NHCH}(-)\text{NHC}(=\text{S})-$, respectively. Various reactions of the supposed carbonium/imonium ion $2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{C}(=\text{S})\text{N}-\text{CH}_2^+ \leftrightarrow 2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{C}(=\text{S})\text{NH}^+=\text{CH}_2$ are described. The results of tests for the pre-emergence and post-emergence herbicidal activities are described and discussed. Most of the compounds show a high preemergence herbicidal activity.

Since the discovery of 2,6-dichlorobenzonitrile as a pre-emergence herbicide by Koopman and Daams (1960), several investigators have searched for derivatives that could generate the nitrile in question, either in the plant or in the soil. (Registered trade marks: "Casoron" and "Casoron 133"; common name: dichlobenil. "Casoron 133" has also been referred to as H 133, 2,6 DBN, and N 5996.)

2,6-Dichlorothiobenzamide was the first compound to be described having a herbicidal activity resembling that of 2,6-dichlorobenzonitrile (Shell Research Ltd., 1963); 2,6-dichlorobenzamide proved to have no herbicidal activity at all.

Generally, all the compounds with an activity like that of 2,6-dichlorobenzonitrile are derivatives of 2,6-dichlorothiobenzamide (Milborrow, 1965), though there are exceptions (Farbenfabriken Bayer A.G., 1965; Koopman, 1961).

To obtain products with an improved uptake of 2,6-dichlorobenzonitrile in plants, we synthesized some chemical formulations of this nitrile by reaction of 2,6-dichlorothiobenzamide with aldehydes.

CHEMISTRY AND ANALYTICAL RESULTS

All melting points are uncorrected. Infrared spectra were measured on a Perkin-Elmer 337 spectrophotometer: method KBr-pellet.

Nuclear magnetic resonance spectra were run on a Varian HA 100 spectrometer. Chemical shifts were measured with tetramethylsilane as internal reference. Microanalyses were carried out at the Analytical Department, Laboratory of Organic Chemistry, University of Groningen under supervision of W. M. Hazenberg.

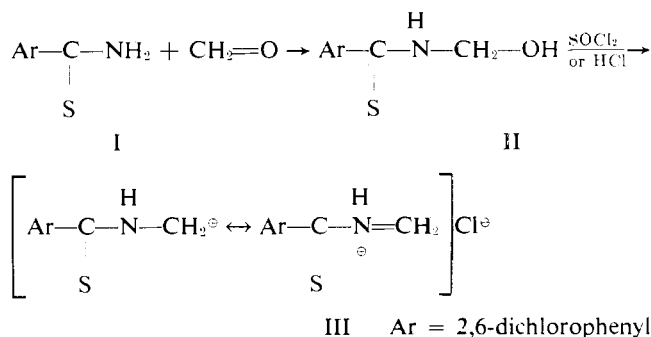
Reactions of 2,6-Dichlorothiobenzamide with Formaldehyde. SYNTHESIS OF *N*-HYDROXYMETHYL-2,6-DICHLOROTHIOBENZAMIDE (II). (Procedure developed by Hans Arnoldy.) A

suspension of 1000 g of 2,6-dichlorothiobenzamide (4.25 moles) in 2000 ml of toluene was heated to 75–85° C. After the addition of 30 ml of water, formaldehyde gas was passed in at the same temperature. The introduction of 153 g of formaldehyde took 2 to 7 hr. While stirring, the warm solution of *N*-hydroxymethyl-2,6-dichlorothiobenzamide was added in 30 min to 4000 ml of petroleum ether (60–80° C). After cooling to 15–25° C the precipitate was collected and washed with 500 ml of petroleum ether (60–80° C).

The yellowish green product was dried *in vacuo* at room temperature; yield 1040–1090 g (90–95%); mp 106–109° C (dec).

A part of it was recrystallized from benzene; mp 112–115° C (dec). *Anal.* Calcd for $\text{C}_8\text{H}_7\text{Cl}_2\text{NOS}$ (236.13): C 40.69; H 2.99; Cl 30.03; N 5.94; S 13.59. Found: C 41.0; H 3.1; Cl 30.3; N 6.2; S 13.6; nmr (DMSO-*d*₆): δ_{NH} 11.00; $\delta_{\text{N}-\text{CH}_2}$ 5.08; δ_{OH} 6.33; $J_{\text{NH}-\text{CH}_2}$ not apparent; $J_{\text{OH}-\text{CH}_2}$ = 7.2 Hz; (CDCl₃): δ_{NH} 8.21; $\delta_{\text{N}-\text{CH}_2}$ 5.22; δ_{OH} 4.30; $J_{\text{NH}-\text{CH}_2}$ = 6.0; $J_{\text{OH}-\text{CH}_2}$ = 8.4 Hz.

N-CHLOROMETHYL-2,6-DICHLOROTHIOBENZAMIDE (III). On treatment with thionyl chloride or hydrogen chloride, compound II gave *N*-chloromethyl-2,6-dichlorothiobenzamide (III), which was a key compound for further synthesis.



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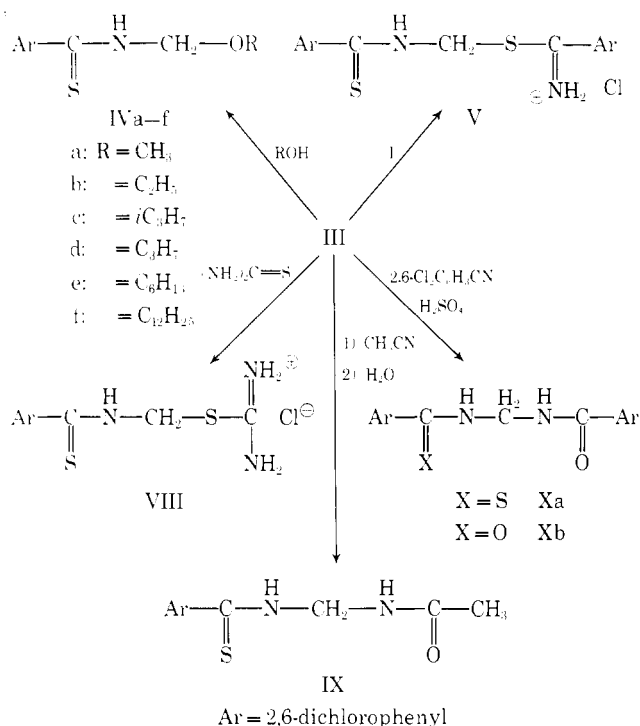
Ross *et al.* (1966) showed that a carbonium/imonium ion of type III is easily formed under acid conditions.

Table I. Compounds IV b-f

Compd. No.	R	Method	Yield %	Mp °C	Analysis, %			
					C	H	Cl	N
IV b	C ₂ H ₅ —	SOCl ₂	31	112-5	Found 45.6; Calcd 45.46	4.3; 4.20	26.7; 26.84	5.2; 5.31
IV c	<i>i</i> C ₃ H ₇ —	HCl	75	119-20	Found 47.6; Calcd 47.49	4.7; 4.71	25.5; 25.49	
IV d	C ₃ H ₇ —	SOCl ₂	14	88-91	Found 47.6; Calcd 47.49	4.8; 4.71	25.5; 25.49	
IV e	C ₆ H ₁₃ —	SOCl ₂	48	55-6	Found 52.5; Calcd 52.49	5.9; 5.99		
IV f	C ₁₂ H ₂₅ —	SOCl ₂	35	42-4	Found 58.7; Calcd 59.39	7.5; 7.73	18.1; 17.53	3.4; 3.47

^a Ar = 2,6-dichlorophenyl.

We were able to couple compound III with some nucleophilic reagents:



N-ALKOXYMETHYL-2,6-DICHLOROTHIOBENZAMIDES (IV a-f). *N*-Methoxymethyl-2,6-dichlorothiobenzamide (IV a) by The Thionyl Chloride Method. A solution of 23.6 g of the *N*-hydroxymethyl compound II (0.10 mole) in 200 ml of dry ether was added from a dropping funnel to a stirred solution of 7.5 ml of thionyl chloride (0.10 mole) in 100 ml of dry ether. The reaction mixture was boiled for 1 hr and, after cooling, filtered from a crystalline product: yield 2.1 g; mp 164-5° C (dec). This product proved to be *S*-(2,6-dichlorothiobenzamidomethyl)-2,6-dichlorothiobenzimidate hydrochloride (V). Three hundred milliliters of methanol was added to the filtrate and the mixture was boiled for another hour. The solvent and the excess of methanol were distilled off until the residue had a volume of 60 ml. On cooling to 5° C the product started to crystallize. The crystals were collected by filtration, washed twice with 50 ml of cold ether, and dried: yield 16.8 g (67%); mp 140-3° C. Anal. Calcd for C₉H₉Cl₂NOS (250.15): C 43.22; H 3.63; Cl 28.35; S 12.82. Found: C 43.4; H 3.8; Cl 28.3; S 13.2.

N-Methoxymethyl-2,6-dichlorothiobenzamide (IV a) by The Hydrochloric Acid Method. Compound II (11.8 g, 0.05 mole) was dissolved in 150 ml of benzene at 20-30° C. This solution was saturated with gaseous hydrogen chloride, after which 150 ml of methanol was added. The reaction mixture was boiled for 45 min, diluted with 200 ml of ether, and washed thoroughly with water. The organic layer was dried over sodium sulfate and concentrated to 75 ml. The product crystallized on cooling: yield 7.4 g (59%); mp 140-3° C. Compounds IV b-f are listed in Table I.

S-(2,6-DICHLOROTHIOBENZAMIDOMETHYL)-2,6-DICHLOROTHIOBENZIMIDATE HYDROCHLORIDE (V). 2,6-Dichlorothiobenzamide (10.3 g, 0.05 mole) was dissolved in 125 ml of hot benzene and 0.75 g of paraform (0.025 mole) was added.

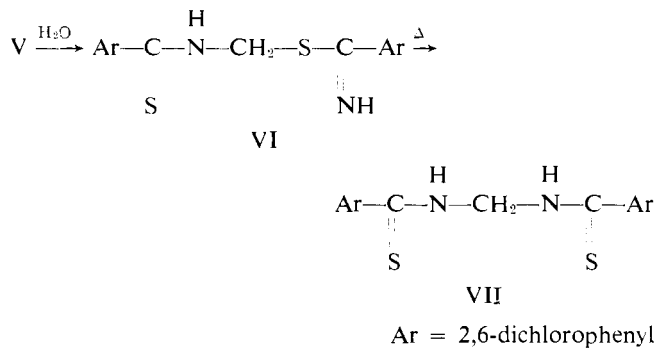
Dry hydrogen chloride was passed in while stirring at a temperature of 50-60° C. Paraform went into solution and 5 min later the product started crystallizing from the solution. The reaction was complete after 90 min. The mixture was cooled and the crystals were collected.

Microanalysis and infrared spectrum showed the product to be a 1:1 complex of compound V with benzene. Therefore the complex was heated *in vacuo* on a steam bath for 2 hr: yield 10.4 g (96%); mp 175-6° C (dec).

Anal. Calcd for C₁₅H₁₁Cl₃N₂S₂ (460.69): C 39.10; H 2.41; Cl 38.48; N 6.08; S 13.92. Found: C 39.2; H 2.5; Cl 38.4; N 6.0; S 13.9.

No nuclear magnetic resonance spectrum of compound V could be recorded, because in all usual solvents it is either insoluble or unstable.

S-(2,6-DICHLOROTHIOBENZAMIDOMETHYL)-2,6-DICHLOROTHIOBENZIMIDATE (VI) AND METHYLENE BIS-(2,6-DICHLOROTHIOBENZAMIDE (VII)).



Thiobenzimidate hydrochloride V (9.2 g, 0.02 mole) was suspended in 200 ml of water and stirred for 2.5 hr at room

temperature. The solid was filtered off, washed with water, and dried *in vacuo*: yield 7.8 g of the thiobenzimidate VI (92%); mp 120.5–2.0° C. *Anal.* Calcd for C₁₅H₁₀Cl₄N₂S₂ (424.23): C 42.47; H 2.37; Cl 33.43; N 6.61. Found: C 42.5; H 2.5; Cl 33.2; N 7.0.

Thiobenzimidate VI (20.0 g, 0.04 mole) was suspended in 200 ml of toluene and heated to reflux for 5 hr. The hot solution was filtered and the filtrate cooled to 20° C. The rearranged product crystallized from its solution. The crystals were collected, washed twice with toluene and petroleum ether (40–60° C) and dried: yield 13.5 g (67.5%) VII; mp 228–33° C.

Anal. Calcd for C₁₅H₁₀Cl₄N₂S₂ (424.23): C 42.47; H 2.37; Cl 33.43; N 6.61; S 15.12. Found: C 42.4; H 2.5; Cl 33.5; N 6.7; S 15.2; nmr VI (DMSO d₆): δ_{C-SNH} 11.58; δ_{N-CH₂} 5.37; very fast decomposition into I (a.o.). (CDCl₃): δ_{C-SNH} 8.77; δ_{N-CH₂} 5.65; J_{NH-CH₂} = 6.4 Hz; slow decomposition. Nmr VII (DMSO d₆): δ_{NH} 11.38; δ_{N-CH₂} 5.52; J_{NH-CH₂} = 5.5 Hz.

S - (2,6 - DICHLOROTHIOBENZAMIDOMETHYL) - ISOTHIURONIUM CHLORIDE (VIII). The *N*-hydroxymethyl compound (II) (23.6 g, 0.10 mole) and 7.6 g of thiourea (0.10 mole) were dissolved in 200 ml of 85% dioxane. Hydrogen chloride was passed in at a temperature of 40–50° C for 4 hr. The solvent was distilled off completely at diminished pressure. The residue was recrystallized from butanol: yield 17.1 g (52%); mp 186–8° C.

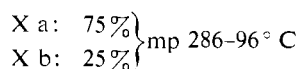
Anal. Calcd for C₉H₁₀Cl₃N₃S₂ (330.70): C 32.69; H 3.05; Cl 32.17. Found: C 33.3; H 3.3; Cl 31.6. (Not quite satisfactory analysis; this may have been caused by some hydrolysis on recrystallization.) Nmr (DMSO d₆): δ_{NH} 11.81; δ_{N-CH₂} 5.41; δ_{C-NH₂·HCl} 9.43; J_{NH-CH₂} = 6.0 Hz.

N - (2,6 - DICHLOROTHIOBENZAMIDOMETHYL) - ACETAMIDE (IX). *N*-hydroxymethyl-2,6-dichlorothiobenzamide (II) (23.6 g, 0.10 mole) was dissolved in 100 ml of acetonitrile and the solution was saturated with hydrogen chloride.

The reaction mixture was poured into 500 ml of water while stirring. After 30 min the crystals were collected, washed with water, and recrystallized from isopropanol: yield 17.2 g (62%); mp 158.0–9.5° C.

Anal. Calcd for C₁₀H₁₀Cl₂N₂OS (277.19): C 43.33; H 3.64; Cl 25.58. Found: C 43.7; H 3.8; Cl 25.5.

FORMATION OF A MIXTURE OF *N*-(2,6-DICHLOROTHIOBENZAMIDOMETHYL)-2,6-DICHLOROBENZAMIDE (Xa) AND METHYLENE BIS-(2,6-DICHLOROBENZAMIDE) (Xb) AND OF 2,6-BIS(2,6-DICHLOROPHENYL)-4H-1,3,5-THIADIAZINE (XI). A solution of 11.8 g of *N*-hydroxymethyl-2,6-dichlorothiobenzamide (II) (0.05 mole) and 8.6 g of 2,6-dichlorobenzonitrile (0.05 mole) in 75 ml of conc sulfuric acid was heated to 75° C for 1 hr. The reaction mixture was poured onto crushed ice and the precipitate collected, washed with water, and dried *in vacuo*. Extraction with 150 ml of hot benzene left behind 2.0 g of crystalline product, consisting of two compounds.

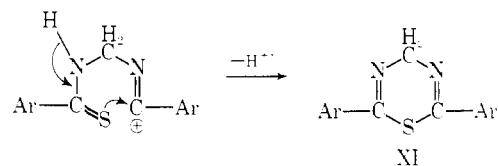


Anal. Calcd for the mixture: C 44.57; H 2.50; Cl 35.13; N 6.95; S 5.89. Found: C 44.8; H 2.7; Cl 35.0; N 6.5; S 6.0. Nmr X a (DMSO d₆): δ_{C=NH} 9.58; δ_{C-SNH} 11.32; δ_{N-CH₂} 5.14; J_{C=NH-CH₂} = 6.2 Hz; J_{C-SNH-CH₂} = 5.8 Hz. X b (DMSO d₆): δ_{NH} 9.48; δ_{N-CH₂} 4.73; J_{NH-CH₂} = 6.2 Hz.

Concentrating and cooling of the benzene layer gave 9.1 g of the crystalline 4H-1,3,5-thiadiazine XI (47%); mp 175–8° C.

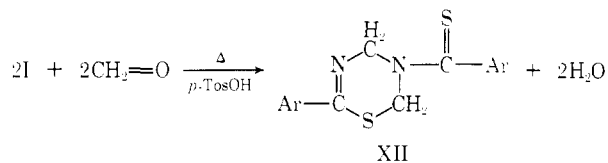
Anal. Calcd for C₁₅H₈Cl₄N₂S (390.14): C 46.18; H 2.07; Cl 36.36; N 7.18; S 8.22. Found: C 46.5; H 2.3; Cl 36.2; N 7.1; S 8.0. Nmr (CDCl₃): δ_{N-CH} 5.72.

We suppose that this 4H-1,3,5-thiadiazine has been formed by the proton loss of the intermediate carbonium ion:



Ar = 2,6-dichlorophenyl

6 - (2,6 - DICHLOROPHENYL) - 3 - (2,6 - DICHLOROTHIOBENZOYL) - 2,3 - DIHYDRO - 4H - 1,3,5 - THIADIAZINE (XII).



Ar = 2,6-dichlorophenyl

2,6-Dichlorothiobenzamide (20.6 g, 0.10 mole), 1 g of *p*-toluene-sulfonic acid and 1 g of paraformaldehyde were dissolved in 300 ml of toluene and heated to reflux.

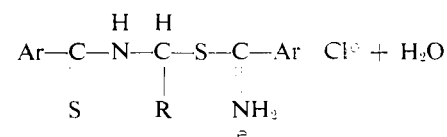
Gaseous formaldehyde was passed in for 5 hr. Water formed during the reaction was trapped in a Dean-Stark apparatus. The solution was concentrated to 150 ml and cooled. The white solid formed was collected and dried: yield 7.8 g (36%); mp 172–4° C.

Anal. Calcd for C₁₆H₁₀Cl₄N₂S₂ (436.23): C 44.05; H 2.31; Cl 32.51; N 6.43. Found: C 43.9; H 2.3; Cl 32.1; N 6.3. Nmr (CDCl₃): δ_{N-CH₂-N} 5.76; δ_{N-CH₂-S} 5.43.

REACTION OF 2,6-DICHLOROTHIOBENZAMIDE WITH OTHER ALIPHATIC ALDEHYDES. *N*-(1-HYDROXY-2,2,2-TRICHLOROETHYL)-2,6-DICHLOROTHIOBENZAMIDE (XIII). 2,6-Dichlorothiobenzamide (4.12 g, 0.02 mole) and 9 ml of chloral (0.09 mole) were dissolved in 40 ml of ether. After standing at room temperature for 3 days, the reaction mixture was washed twice with a solution of sodium hydrogencarbonate, dried over sodium sulfate, and evaporated to dryness. The oily residue was crystallized from carbon tetrachloride; yield 4.40 g (62.5%); mp 98–101° C.

Anal. Calcd for C₉H₆Cl₅NOS (353.50): C 30.57; H 1.71; Cl 50.15. Found: C 31.3; H 1.9; Cl 50.1.

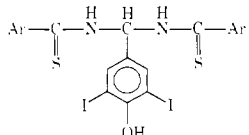
S - [I - (2,6 - DICHLOROTHIOBENZAMIDO)ALKYL] - 2,6 - DICHLOROTHIOBENZIMIDATE. HYDROCHLORIDES (XIV a-c).



XIV a-c XIV a: R = CH₃
Ar = 2,6-dichlorophenyl b: R = C₂H₅
c: R = C₃H₇

S - [I - (2,6 - DICHLOROTHIOBENZAMIDO)ETHYL] - 2,6 - DICHLOROTHIOBENZIMIDATE HYDROCHLORIDE (XIV a). 2,6-Dichlorothiobenzamide (20.6 g, 0.10 mole) and 2.25 ml of paraldehyde (0.05 mole of acetaldehyde) were dissolved in 960 ml of benzene. Gaseous hydrogen chloride was passed in at

Table II. Compound XIV b,c and XV a,b

Compd. No.	Formula	Yield %	Mp °C		Analysis, %			N	S	
					C	H	Cl			
XIV b	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{Ar}-\text{C}-\text{N}-\text{C}-\text{S}-\text{C}-\text{Ar} \text{ Cl}^- \\ \quad \quad \\ \text{S} \quad \text{C}_2\text{H}_5 \quad \text{NH}_2^- \end{array}$	91	147-8 (dec)	Found Calcd	42.2 41.79	3.2 3.10	35.8 36.28			
XIV c	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{Ar}-\text{C}-\text{N}-\text{C}-\text{S}-\text{C}-\text{Ar} \text{ Cl}^- \\ \quad \quad \\ \text{S} \quad \text{C}_5\text{H}_{11} \quad \text{NH}_2^- \end{array}$	45	107-111 (dec)	Found Calcd	44.9 45.26	3.6 3.99	32.6 33.40			
XV a	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{Ar}-\text{C}-\text{N}-\text{C}-\text{N}-\text{C}-\text{Ar} \\ \quad \quad \\ \text{S} \quad \text{Ar} \quad \text{S} \end{array}$	37	102-4	Found Calcd	44.6 44.31	2.4 2.12	35.3 37.37			
XV b		47.5	205-6	Found Calcd	32.9 32.84	1.9 1.57	halogen halogen	51.2 51.51	3.5 3.65	8.1 8.35

^a Ar = 2,6-dichlorophenyl.

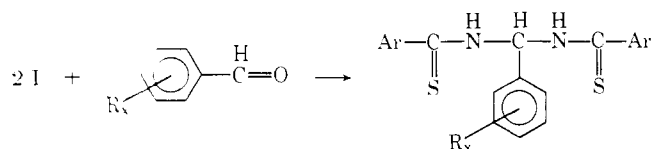
30° C for 1 hr. The product separated as an oil, which crystallized overnight. The crystals were collected and washed with benzene and petroleum ether (40-60° C). The product was dried *in vacuo* over P₄O₁₀; yield 23.6 g (100%) of XIV a; mp 140-2° C (dec).

Anal. Calcd for C₁₆H₁₀Cl₃N₂S₂ (474.52): C 40.49; H 2.76; Cl 37.36; N 5.91. Found: C 40.6; H 2.9; Cl 36.9; N 5.9.

The thiobenzimidate hydrochlorides XIV b and c, which were prepared in the same way, using propanal and hexanal, respectively, instead of paraldehyde, are listed in Table II.

In contrast with the thiobenzimidate hydrochloride (V), these compounds are very sensitive to hydrolysis. The addition of water causes a quick breakdown to 2,6-dichlorobenzonitrile. This made it impossible to rearrange the compounds XIV a-c to the symmetrical bis-thiobenzamides.

Reaction of 2,6-Dichlorothiobenzamide with Two Substituted Benzaldehydes.



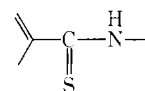
V a: R_x = 2,6-dichloro
 b: R_x = 3,5-diiodo-4-hydroxy
 Ar = 2,6-dichlorophenyl

2,6-Dichlorobenzylidene-bis(2,6-dichlorothiobenzamide) (XV a). This was prepared according to procedure XIV a. The reaction mixture was heated with reflux for 2.5 hr. The water formed was trapped in a Dean-Stark apparatus.

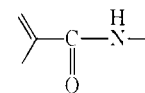
3,5-Diiodo-4-hydroxybenzylidene-bis(2,6-dichlorothiobenzamide) (XV b). This was also prepared by the procedure for XIV a. The reaction mixture was heated at 40° C for 100 hr. The crude product was crystallized from methanol. Nmr (DMSO d₆): δ_{NH} 11.53; δ_{NCH} 8.08; δ_{C₆H₃OH} 7.94; δ_{OH} 9.70; J_{NH-CH} = 7.5 Hz. Compounds XV a and XV b are listed in Table II.

DISCUSSION OF ANALYTICAL RESULTS

Nuclear Magnetic Resonance Spectra. The thioamide function could always be identified by the chemical shift of the



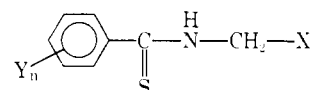
NH proton in DMSO d₆ (δ 11.0-δ 11.8), which differs from the chemical shift of the amide function



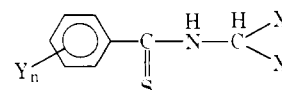
(about δ 9.5). Both the NH protons do not exchange after addition of trifluoroacetic acid.

Infrared Spectra. In general, wide frequency ranges for the characteristic thioamide absorptions are indicated in literature to limit their use for structure analysis.

The environment of the thioamide function strongly affects the characteristic absorption, making the frequency ranges very wide. We analyzed a number of thioamides of the general structure



and found two characteristic bands in a much smaller range: 1500 to 1550 cm⁻¹ (strong and broad) and 937 to 962 cm⁻¹ (medium to strong). These absorptions lie within or near to the ranges quoted in literature. In thioamides of the general



structure the absorption near 950 cm⁻¹ is missing sometimes, while the strong absorption near 1520 cm⁻¹ does not disappear.

The structure of *N*-hydroxymethyl-2,6-dichlorothiobenz-

Table III. The Herbicidal Activities of the Compounds

Compd. No.	Formula Ar = 2,6-dichlorophenyl	Inhibition of germination ^a 10 kg/ha										Phytotoxicity ^b 10 kg/ha						Watering of the roots of oats 60 kg/ha	
		Si	P	Sm	Pa	Lep	Ph	Sl	Av	Sm	B	Sp	U	Se	Al	Ga	Pc		C
II	$\begin{matrix} \text{H} \\ \\ \text{Ar}-\text{C}-\text{N}-\text{CH}_2-\text{OH} \\ \\ \text{S} \end{matrix}$	++	++	++	++	++	6	6	3	6	6	6							†
IV a	$\begin{matrix} \text{H} \\ \\ \text{Ar}-\text{C}-\text{N}-\text{CH}_2-\text{O}-\text{CH}_3 \\ \\ \text{S} \end{matrix}$	+	++	++	++	+	0	2	2	2	2	2							68
IV b	$\begin{matrix} \text{H} \\ \\ \text{Ar}-\text{C}-\text{N}-\text{CH}_2-\text{O}-\text{C}_3\text{H}_5 \\ \\ \text{S} \end{matrix}$	+	++	++	±	++	3	3	2	3	3	4	6	4	3				39
IV c	$\begin{matrix} \text{H} \\ \\ \text{Ar}-\text{C}-\text{N}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_7 \\ \\ \text{S} \end{matrix}$	++	++	++	++	++	1	2	2	2	2	2	6	4	1				†
IV d	$\begin{matrix} \text{H} \\ \\ \text{Ar}-\text{C}-\text{N}-\text{CH}_2-\text{O}-\text{C}_3\text{H}_7 \\ \\ \text{S} \end{matrix}$	++	++	++	++	++	3	3	2	4	4	4	6	4	3				14
IV e	$\begin{matrix} \text{H} \\ \\ \text{Ar}-\text{C}-\text{N}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_{13} \\ \\ \text{S} \end{matrix}$	-	++	++	-	++	2	1	1	2	1	4	4	3	1	1	1	3	†
IV f	$\begin{matrix} \text{H} \\ \\ \text{Ar}-\text{C}-\text{N}-\text{CH}_2-\text{O}-\text{C}_{12}\text{H}_{25} \\ \\ \text{S} \end{matrix}$	-	+	++	-	-	2	0	2	2	1	2	3	2	1	3	1	2	28
V	$\begin{matrix} \text{H} \\ \\ \text{Ar}-\text{C}-\text{N}-\text{CH}_2-\text{S}-\text{C}-\text{Ar}-\text{HCl} \\ \quad \\ \text{S} \quad \text{NH} \end{matrix}$	+	++	++	++	++	2	2	1	1	3	1	5	5	4				21
VI	$\begin{matrix} \text{H} \\ \\ \text{Ar}-\text{C}-\text{N}-\text{CH}_2-\text{S}-\text{C}-\text{Ar} \\ \quad \\ \text{S} \quad \text{NH} \end{matrix}$	++	++	++	+	++	0	0	1	0	0	1	4	3	4	0	1	0	†
VII	$\begin{matrix} \text{H} \\ \\ \text{Ar}-\text{C}-\text{N}-\text{CH}_2-\text{N}-\text{C}-\text{Ar} \\ \quad \quad \\ \text{S} \quad \text{S} \end{matrix}$	-	++	++	+	-	0	0	1	0	0	1	3	3	0	0	2	0	100
VIII	$\begin{matrix} \text{H} \\ \\ \text{Ar}-\text{C}-\text{N}-\text{CH}_2-\text{S}-\text{C}-\text{NH}_2-\text{HCl} \\ \quad \\ \text{S} \quad \text{NH} \end{matrix}$	+	++	++	+	++	1	1	1	2	3	3	3	2	1	1	1	2	†

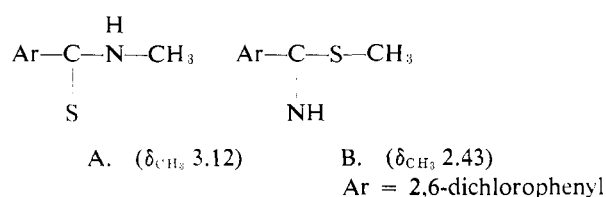
amide was determined by nmr and ir. S-Hydroxymethylation was excluded by nmr. A spin coupling of the —OH and —NH protons with the methylene protons is apparent. In ir the presence of the characteristic bands of the thioamide function was demonstrated.

The infrared spectrum of V showed the characteristic bands of the thioamide group and of the group $\text{NH}_x^{\oplus}\text{Cl}^{\ominus}$.

The composition of the mixture of X a and X b was determined by nmr and microanalysis.

The free base VI demonstrated its structure more easily than its salt, because in solution it is more stable. In ir two ν NH bands are present. One of them ($=\text{NH}$) is insensitive to change of state (solid \rightarrow solution), indicating a very low hydrogen bonding ability, as is also indicated by the easy loss of hydrochloric acid from the salt.

The value of the chemical shift of the CH_2 doublet [due to coupling with $-\text{C}(=\text{S})\text{NH}$], calculated with Shooley additivity using the methyl chemical shifts of the model compounds (A) and (B), fits very well the observed one (calcd δ 5.1, observed δ 5.37).



For the 2,6-dichlorophenyl group we observed a multiplet near δ 7.4 in all cases.

TEST METHODS

The tests performed to determine the herbicidal properties of the compounds have been described in one of our previous publications on herbicides (van Daalen *et al.*, 1967).

TEST RESULTS AND DISCUSSION

The test results listed in Table III indicate that an impressive number of the compounds show high herbicidal activities, obviously due to the generation of 2,6-dichlorobenzonitrile. Compounds showing no herbicidal properties are evidently not broken down to 2,6-dichlorobenzonitrile, *e.g.* compounds X, XI and XII.

It is remarkable that compounds IX and VII exhibit a moderate to high herbicidal activity, contrary to the unexplainable lack of activity of compound X, which has a similar structure.

The first group of compounds II-IV f exerts very strong effects, which in the case of the alkoxy derivatives can be attributed to the formation of 2,6-dichlorobenzonitrile by microbiological degradation, no activity having been found in sterilized soil.

Compounds V and VI are structurally very similar, V being the hydrochloride of VI. They show appreciable differences in activity when applied at low concentrations, *e.g.* 1 to 3 kg per hectare. Compound V shows rapid and strong effects, and compound X shows slow but long-lasting herbicidal activities. This discrepancy can only be explained by a difference in the water-solubility of the compounds.

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