trum of this material showed bands at 7.95 (Si–CH_3), 8.10 (Si–C_2H_5), and 9.35 μ (Si–O).

Anal. Calcd. for $C_{10}H_{26}Si_2O$: C, 55.04; H, 11.92. Found: C, 54.94; H, 11.92.

An authentic sample of this disiloxane was prepared from diethyldichlorosilane and methylmagnesium bromide. The two samples showed identical physical and spectral properties.

C. **(α-Chloroethyl)dimethylethylsilane.**—Direct chlorination[2] of 264 g. (1.68 moles) of diethyldichlorosilane yielded 56.8 g. (17.6%) of (α-chloroethyl)ethyldichlorosilane, b.p. 160–165°, $n^{28}D$ 1.4541–1.4575 (lit.[13] b.p. 160°); 34.6 g. (11%) of (β-chloroethyl)ethyldichlorosilane, b.p. 175–183°, $n^{23}D$ 1.4621–1.4645 (lit.[13] b.p. 178°); and 104 g. (25%) of recovered diethyldichlorosilane. Treatment of the (α-chloroethyl)ethyldichlorosilane (56.8 g., 0.29 mole) with 1.34 moles of methylmagnesium bromide followed by water work-up and distillation yielded 27.1 g. (53%) of (α-chloroethyl)dimethylethylsilane, b.p. 143–145°, $n^{24}D$ 1.4340. A redistilled sample, b.p. 144–144.5°, $n^{24}D$ 1.4341, was used for analysis.

Anal. Calcd. for $C_6H_{15}SiCl$: C, 47.84; H, 9.96; Cl, 23.58. Found: C, 47.70; H, 9.69; Cl, 23.88.

A mixture of 13.5 g. (0.09 mole) of the (α-chloroethyl)silane and 23.0 g. (0.18 mole) of quinoline was heated at reflux for 24 hr. The material boiling up to 200° was removed by direct distillation of the reaction mixture. Fractional distillation of this material yielded 9.5 g. (70%) of recovered (α-chloroethyl)dimethylethylsilane, b.p. 142–143°, $n^{25}D$ 1.4302. Only 0.2 g. of material boiling in the range of 85–95°, $n^{26}D$ 1.4012, was obtained. Gas phase analysis revealed that this fraction consisted of one major component which had a retention time the same as that of an authentic sample of vinylethyldimethylsilane, b.p. 88°, $n^{25}D$ 1.4062, prepared in 35% yield by the method of Sommer (lit.[13] b.p. 88°, $n^{25}D$ 1.4089).

D. **(Chloro)silacyclopentanes. 1. Mixture of Isomers.**—To a 50-g. mixture of 1-chloromethyl-1-methylsilacyclopentane (**2**) and 1,1-dimethyl-2-chlorosilacyclopentane[14] (**3**), was added 110.0 g. (0.85 mole) of quinoline. The resulting solution was heated at reflux for 2 hr. and distilled to remove material boiling up to 210°. The milky white distillate was washed carefully with 6 *N* hydrochloric acid, diluted with ether, washed with water, and finally dried with potassium carbonate. Fractional distillation yielded 2.9 g. (*ca.* 15%) of 1,1-dimethylsilacyclo-2-pentene (**7**), b.p. 94–100°, $n^{25}D$ 1.4439 (lit.[15] b.p. 100–106°, $n^{24}D$ 1.4425); 11.3 g. (*ca.* 45%) of 1,1-dimethyl-2-chlorosilacyclopentane (**3**) (previously assigned structure **1**[2]), b.p. 158°, $n^{25}D$ 1.4687; and 7.1 g. (*ca.* 40%) of *sym*-dimethylbis(cyclotetramethylene)disiloxane (**8**), b.p. 215–217°, $n^{23}D$ 1.4615 (lit.[5] b.p. 221°, $n^{26}D$ 1.4573). The infrared spectrum of this disiloxane was identical with that of an authentic sample, prepared in 24% yield, using the method of West.[5]

2. **1,1-Dimethyl-2-chlorosilacyclopentane** (**3**).—To 52.0 g. (0.40 mole) of quinoline was added 20.0 g. (0.135 mole) of the 2-chlorosilacyclopentane **3**, isolated as in part D, and the mixture was heated at reflux for 6 hr. Direct distillation followed by fractional distillation yielded 3.0 g. (20%) of 1,1-dimethylsilacyclo-2-pentene (**7**),[15] b.p. 97–100°, $n^{22}D$ 1.4438; and 1.7 g. (10%) of recovered starting material, b.p. 153–158°, $n^{22}D$ 1.4650.

N.m.r. Spectra. A. 1-Chloromethyl-1-methylsilacyclopentane (**2**).—**2** was isolated from the mixture of isomers using a 15 ft. × 1/8 in. 20% silicone preparative gas chromatographic column,[16] $n^{22}T$ 1.4741.

Anal. Calcd. for $C_6H_{13}SiCl$: C, 48.46; H, 8.81; Cl, 23.81. Found: C, 48.43; H, 8.77; Cl, 23.68.

The n.m.r. spectrum[9] showed the following bands (p.p.m.): 0.02 (singlet), 0.65 (unresolved multiplet), 1.60 (pentuplet), and 2.75 (singlet). The integrated areas under these peaks appeared in the ratios of 2.8:4.0:4.0:2.0, which are in agreement with the expected ratios of 3:5:4:2.

B. **1,1-Dimethyl-2-chlorosilacyclopentane** (**3**).—The n.m.r. spectrum[9] was run on the sample isolated from reaction D1. The following bands were observed (p.p.m.): 0.15 (singlet), 0.25 (singlet), 0.65 (unresolved multiplet), 1.85 (unresolved multiplet), and 3.30 (triplet). The ratios of the integrated areas under the peaks (2.9:3.0:2.0:4.0:1.2) are in agreement with the expected ratios 3:3:2:4:1.

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[13] L. H. Sommer, D. L. Bailey, G. M. Goldberg, D. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954).

[14] (a) Gas phase chromatography at 150° indicated that the mixture was composed of an approximately equal ratio of the two α-chloro isomers. In contrast to our previous work, this mixture was distilled prior to the quinoline reflux to remove any higher-boiling disiloxanes which would be expected to arise from the hydrolysis of the 3-chlorodimethylsilacyclopentane during water work-up. (b) Yields are based upon the estimated weight of the isomer in the mixture.

[15] (a) R. J. Fessenden and F. J. Freenor, *J. Org. Chem.*, **26**, 2003 (1961). (b) V. F. Mironov and V. V. Nepomnia, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1231 (1959); *Chem. Abstr.*, **54**, 1268 (1960). (c) Three attempts to analyze for carbon and hydrogen were prevented by explosions during combustion. The reason for this behavior is not apparent.

[16] Specially prepared for the Aerograph Model A-90-C by the Wilken Instrument and Research Co., Walnut Creek, Calif.

Reactions of Enamines. III.[1] Chlorothionacetamides

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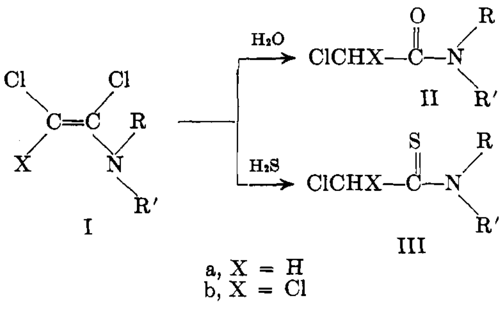
Received June 26, 1963

A synthesis of α-chloro- and α,α-dichlorothionacetamides by reaction of 1,2-dichloro- and 1,2,2-trichlorovinylamines with hydrogen chloride–hydrogen sulfide is reported. A similar reaction of 1,2,2-trichlorovinylamines with chlorine–hydrogen sulfide produces trichlorothionacetamides. The ultraviolet, infrared, and n.m.r. spectra of the thionamides and the mechanism of their formation are discussed.

The hydrolysis of N,N-disubstituted 1,2-dichlorovinylamines (Ia) or 1,2,2-trichlorovinylamines (Ib) has been shown to yield the corresponding chloro- and dichloroacetamides (IIa and IIb), respectively.[2]

Since this reaction leads to high yields of chloroacetamides at low temperatures, the analogous reaction with hydrogen sulfide appeared to be a promising method for the preparation of the unreported N-substituted α-chlorothionacetamides (III).



a, X = H
b, X = Cl

The recent preparations of α-chlorothionacetamide and α,α,α-trichlorothionacetamide by reaction of the respective nitriles with thionophosphoric acid derivatives followed by treatment with hydrogen chloride

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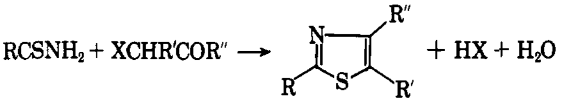
[1] For paper II of this series, see A. J. Speziale and G. H. Alt, *Tetrahedron Letters*, **No. 2**, 111 (1963).

[2] (a) A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 909 (1960); (b) A. J. Speziale and L. R. Smith, *ibid.*, **84**, 1868 (1962).

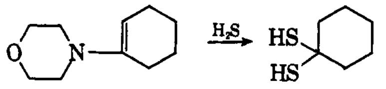
appear to be the only successful syntheses of α-halothionacetamides.[3] These reactions and other methods[4] are applicable only to the conversion of nitriles to primary thionamides. The absence of N-substituted α-halothionacetamides from the literature is probably due to the difficulty of synthesis and to their inherent instability. The usual methods for the conversion of an amide to a thionamide by means of a reactive sulfide such as phosphorus pentasulfide are undesirable for α-halothionamides since such reagents appear to produce reactions involving the α-halogen atom. Similar limitations apply to other methods[4] employing amines (Willgerodt-Kindler reaction, treatment of thiono esters with amines, etc.).

Thionamides condense with α-halocarbonyl compounds[5] to form thiazoles (IV) by nucleophilic displacement of the α-halogen atom by the sulfur atom of the thionamide. Polymerization of α-halothionamides

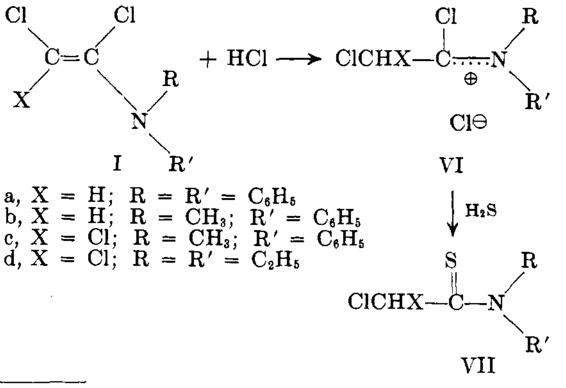

IV

could take place by a similar displacement. It appeared, therefore, that any successful synthesis of N-substituted halothioamides must involve product formation and isolation at low temperatures and as free from contaminants as possible. The reaction of haloenamines with hydrogen sulfide showed promise of fulfilling these requirements.

Although Djerassi[6] reported that enamines react with hydrogen sulfide to give *gem*-dithiols (V), the 1-chloroenamines would not be expected to produce similar results since the chloride ion would be expelled in preference to the amine.


V

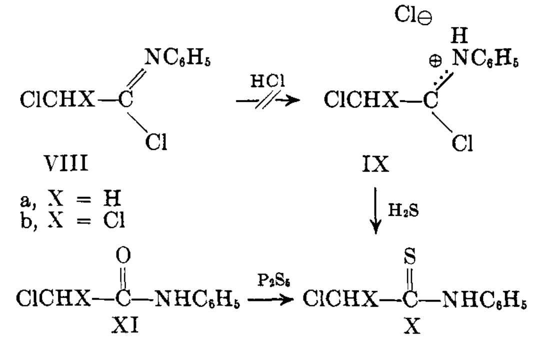
Reaction of N,N-diphenyl-1,2-dichlorovinylamine (Ia) with hydrogen sulfide led to a 72% recovery of the starting chloroenamine. In the presence of hydrogen chloride, however, this reaction led to an 88% yield of N,N-diphenyl-α-chlorothionacetamide (VIIa). The preparations of N-methyl-α-chlorothionacetanilide (VIIb), N-methyl-α,α-dichlorothionacetanilide (VIIc), and N,N-diethyl-α,α-dichlorothionacetamide (VIId) were accomplished in a similar manner.



a, X = H; R = R′ = C_6H_5
b, X = H; R = CH_3; R′ = C_6H_5
c, X = Cl; R = CH_3; R′ = C_6H_5
d, X = Cl; R = R′ = C_2H_5

Reactions of chloroenamines with nucleophiles have been shown to occur *via* iminium salts VI.[2] The failure of hydrogen sulfide to react with chloroenamines in the absence of hydrogen chloride is additional evidence of this fact. Hydrogen sulfide, being a very weak acid, is incapable of protonating the enamines and the addition of hydrogen chloride was, therefore, necessary. Evidently the mechanism of reaction of hydrogen sulfide with VI is similar to that proposed[2] for water.

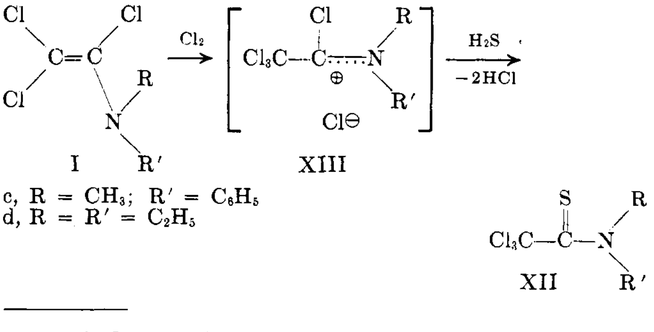
An attempt to extend this reaction to the preparation of N-monosubstituted chlorothionacetamides (X) was not successful. Treatment of N-phenyl-α-chloroacetimidoyl chloride (VIIIa) with hydrogen chloride–hydrogen sulfide led only to decomposition products. A similar reaction with N-phenyl-α,α-dichloroacetimidoyl chloride (VIIIb) produced a 79% recovery of the starting imidoyl chloride. It appears that the iminium salt IX is also necessary for the reaction of imidoyl chlorides with hydrogen sulfide. The dichloroimidoyl chlorides are not sufficiently basic, in contrast to the chloroenamines, to undergo protonation.



a, X = H
b, X = Cl

The synthesis of α,α-dichlorothionacetanilide (Xb) was accomplished by treatment of α,α-dichloroacetanilide (XIb) with phosphorus pentasulfide. N-Methyl-α,α,α-trichloroacetanilide and α,α,α-trichloroacetanilide would not undergo this reaction. Under mild conditions no reaction occurred and under forcing conditions decomposition products were isolated. In the case of the N-methyl derivative, dechlorination took place and a small yield of N-methyl-α,α-dichlorothionacetanilide (VIIc) was isolated.

The N,N-disubstituted trichlorothionacetamides (XII) were prepared by chlorination of the trichlorovinylamines followed by reaction with hydrogen sulfide. This reaction is analogous to the reaction of hydrogen chloride–hydrogen sulfide with the haloenamines and



c, R = CH_3; R′ = C_6H_5
d, R = R′ = C_2H_5

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(3) H. Schicke and G. Schrader (to Farbenfabriken Bayer Aktiengesellschaft), German Patent 1,111,172 (February 13, 1960).

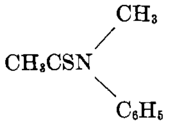
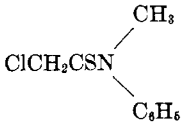
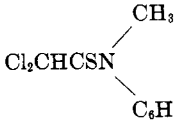
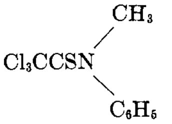
(4) R. N. Hurd and G. De La Mater, *Chem. Rev.*, **61**, 45 (1961).

(5) (a) J. Sprague and A. Land, "Heterocyclic Compounds," R. C. Elderfield, Ed., Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1957, Chap. 8; (b) R. Wiley, D. England, and L. Behr, "Organic Reactions," R. Adams, Ed., Coll. Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 8.

(6) C. Djerassi and B. Tursch, *J. Org. Chem.*, **27**, 1041 (1962).

TABLE I

PHYSICAL CONSTANTS OF THIONAMIDES

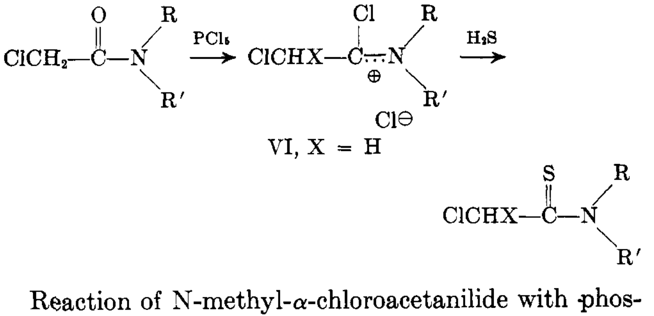
Compound	$-\overset{S}{\overset{\|}{C}}-N<$, infrared, λ cm.⁻¹	M.p., °C.	Ultraviolet, λ_{max}^{EtOH} mμ (log ε)	N.m.r., τ, CCl_4
 $CH_3CSN(CH_3)C_6H_5$	1124[a]	56–58	276 (4.24), 223[e](3.61)	2.67, 6.33, 7.68
 $ClCH_2CSN(CH_3)C_6H_5$	1096[b]	38–39.5	290 (4.04)	2.68, 6.34, 5.83
 $Cl_2CHCSN(CH_3)C_6H_5$	1109[a]	103	297 (3.98), 232 (3.44)	2.58, 6.32, 3.72
 $Cl_3CCSN(CH_3)C_6H_5$	1116[a]	71–72	303 (4.01), 228[e](4.00)	2.70, 6.24
$ClCH_2CSN(C_6H_5)_2$	1115[c]	140–147		
$Cl_2CHCSN(C_2H_5)_2$	1079[b]	[d]	298 (4.17), 231 (3.66)	
$Cl_3CCSN(C_2H_5)_2$	1138[b]	[d]	305 (4.00)	
$CH_3CSNHC_6H_5$	1150[a]	75–76	301 (4.10), 218 (4.15)	2.34–2.76, 7.48,[f] 7.58[f]
$Cl_2CHCSNHC_6H_5$	1093[c]	71–72	318 (3.94), 219 (4.12)	
CH_3CSNH_2	969[c]	115–116	271 (4.66), 217[e](4.63)	

[a] $CHCl_3$ [b] Film. [c] Nujol. [d] Liquid. [e] Inflection. [f] 30°.

constitutes a unique method of formation of iminium salts XIII.

This sequence involves the chlorination of an enamine and is the first reported reaction of this kind. The bromination of enamines has been reported.[7]

We have been investigating the formation of iminium salts VI by the reaction of amides with a variety of reagents including phosphorus pentachloride.[8] These iminium salts should undergo reaction with hydrogen sulfide in the same manner as those produced by protonation of enamines.



VI, X = H

Reaction of N-methyl-α-chloroacetanilide with phosphorus pentachloride followed by treatment with hydrogen sulfide gave N-methyl-α,α-dichlorothionacetanilide (VIIc). It appears that phosphorus pentachloride, in addition to forming the iminium salt VI (X = H), effected α-chlorination. A similar reaction with N-methylacetanilide led to dichlorination and again N-methyl-α,α-dichlorothionacetanilide (VIIc) was isolated.[9]

Since N-methyl-α,α,α-trichloroacetanilide cannot undergo α-chlorination, its reaction with phosphorus pentachloride and hydrogen sulfide should lead to the trichlorothionacetamide. Only the starting trichloroamide, however, was recovered from this reaction. Similar results were obtained with N-methyl-α,α-dichloroacetanilide. It may be that the low nucleophilicity of the di- and trichloroamides as well as steric factors preclude reaction with phosphorus pentachloride.

It appeared worthwhile to examine the spectral properties of these new chlorothionamides and to relate these with the corresponding nonhalogenated thionamides. These data are presented in Table I.

Thiobenzanilide appears to be the only thionamide whose ultraviolet spectrum has been reported.[10]

The ultraviolet spectra of the thionamides exhibit absorption at 271–318 mμ (log ε 3.94–4.66) with the N-monosubstituted thionamides falling in the upper part of the range. The introduction of an α-chlorine atom exerts a bathochromic effect and successive introduction of α-chlorine atoms produce smaller bathochromic shifts.

The similarity of the spectra of thionacetanilide, which could exist as a thiol tautomer XIV, and N-methylthionacetanilide, which could not tautomerize, seems to indicate that thionacetanilide exists predominantly in the thione form. A similar conclusion has been reached by May[10] on examination of the visible spectra of these compounds.

The infrared absorption in the region around 1100

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(7) (a) R. L. Pederson, J. L. Johnson, R. P. Holysz, and A. C. Ott, *J. Am. Chem. Soc.*, **79**, 1115 (1957); (b) M. E. Kuehne, *ibid.*, **83**, 1492 (1961).

(8) A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **27**, 4361 (1962).

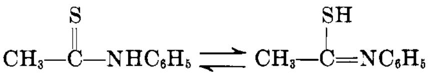
(9) We have reported that reaction of dichloracetamides with phosphorus pentachloride gave 1,2,2-trichlorovinylamines[8] and that the reaction of hydrogen chloride with trichlorovinylamines gave the iminium salts VI.[3]

(10) P. May, *J. Chem. Soc.*, **103**, 2272 (1913).

cm.$^{-1}$ agrees with that reported[11] for thionamides. Bands around 1380 and 1460 cm.$^{-1}$ are also generally present.

The n.m.r. spectrum of N-methylthionacetanilide exhibits complex absorption centered at 2.67 due to the five aromatic protons, a singlet due to the N-methyl group at 6.33 (three protons), and a singlet arising from the α-methyl group at 7.68 τ (three protons). The aromatic and N-methyl absorptions of N-methyl-α-chlorothionacetanilide (2.68, 6.34), N-methyl-α,α-dichlorothionacetanilide (2.58, 6.34), and N-methyl-α,α,α-trichlorothionacetanilide (2.70, 6.24) remain relatively constant but the absorptions due to the α-methyl group are shifted to 5.83 (two protons) and 3.72 τ (one proton). N-Methyl-α,α,α-trichlorothionacetanilide shows only two absorptions as would be expected.

In order to verify that the 7.68 absorption of N-methylthionacetanilide was due to the α-protons, the n.m.r. spectrum of thionacetanilide was examined and found to exhibit absorptions at 7.48 and 7.58 in addition to complex absorption in the region 2.34 to 2.76 τ. The absorptions at 7.48 and 7.58 are in close agreement with that found for N-methylthionacetanilide (7.68 τ) and it must be concluded that these absorptions are due to the α-protons. It is probable that the two absorptions in the 7.5 τ region which are shown by thionacetanilide are due to the methyl groups of tautomers XIV and XV. The two absorptions are quite distinct at 30° but they unite into one band at 50° indicating that only the most stable isomer is present at 50° and above or that the tautomerization is too rapid to be detected at 50°.[12]



$$CH_3-\overset{\overset{S}{\|}}{C}-NHC_6H_5 \rightleftharpoons CH_3-\overset{\overset{SH}{|}}{C}=NC_6H_5$$

XV XIV

The chlorothionacetamides are yellow solids or undistillable oils which vary in stability from the quite stable trichloro derivatives to the unstable monochloro compounds. The presence of aromatic groups on the nitrogen atom has a large stabilizing effect. The compounds are quite unstable to light and must be stored in the dark.

Experimental[13]

N,N-Diphenyl-α-chlorothionacetanilide (VIIa).—A solution of N,N-diphenyl-1,2-dichlorovinylamine (4.1 g., 0.0165 mole) in methylene chloride (70 ml.) was stirred and saturated with hydrogen chloride. Hydrogen sulfide was passed through the solution for 1 hr. and the methylene chloride was removed *in vacuo*. Recrystallization of the residue from methylene chloride–hexane gave N,N-diphenyl-α-chlorothionacetanilide as a yellow solid (3.8 g., 0.00145 mole, 88%), m.p. 140–147° dec.

Anal. Calcd. for $C_{14}H_{12}ClNS$: C, 64.23; H, 4.62; Cl, 13.55; N, 5.35; S, 12.25. Found: C, 63.63; H, 4.89; Cl, 13.58; N, 6.11; S, 11.96.

N-Methyl-α-chlorothionacetanilide (VIIb).—A solution of N-methyl-N-phenyl-1,2-dichlorovinylamine (1.5 g., 0.0068 mole) in methylene chloride (50 ml.) was stirred and saturated with hydrogen chloride for 0.25 hr. Hydrogen sulfide was passed through the solution for 0.5 hr. and the methylene chloride was removed *in vacuo*. The orange oily residue was dissolved in methylene chloride and placed on a column of neutral alumina (Woelm) packed wet with pentane. Elution with methylene chloride gave a yellow oil. This procedure was repeated and elution with methylene chloride gave N-methyl-α-chlorothionacetanilide as a yellow oil which solidified on standing (0.45 g., 0.0023 mole, 34%), m.p. 38–39.5°.

Anal. Calcd. for $C_9H_{10}ClNS$: C, 54.13; H, 5.05; Cl, 17.76; N, 7.02; S, 16.06. Found: C, 54.29; H, 5.19; Cl, 17.25; N, 6.52; S, 15.71.

N-Methyl-α,α-dichlorothionacetanilide (VIIc). A. From N-Methylacetanilide.—A mixture of N-methylacetanilide (3.0 g., 0.02 mole), phosphorus pentachloride (8.3 g., 0.04 mole), and carbon tetrachloride was refluxed for 6 hr. A white solid separated and redissolved. The resulting solution was evaporated to dryness *in vacuo* and the residue dissolved in methylene chloride. Hydrogen sulfide was passed through the solution for 0.25 hr. and the solution was evaporated to dryness *in vacuo*. The residue was dissolved in benzene and placed on a column of neutral alumina packed wet with pentane. Elution with pentane gave N-methyl-α,α-dichlorothionacetanilide (0.72 g., 0.0031 mole, 13%), m.p. 103°.

Anal. Calcd. for $C_9H_9Cl_2NS$: C, 46.16; H, 3.87; Cl, 30.28; N, 5.98; S, 13.70; mol. wt., 234.15. Found: C, 46.23; H, 3.82; Cl, 30.19; N, 5.61; S, 13.43; mol. wt., 259 in benzene (some decomposition).

B. From N-Methyl-α-chloroacetanilide.—A mixture of N-methyl-α-chloroacetanilide (4.6 g., 0.025 mole), phosphorus pentachloride (5.2 g., 0.025 mole), and carbon tetrachloride (40 ml.) was refluxed for 1 hr. Hydrogen chloride was evolved. The clear solution was evaporated to dryness *in vacuo*, the residue dissolved in methylene chloride (40 ml.), and hydrogen sulfide was passed through the solution for 0.25 hr. The residue, after evaporation to dryness *in vacuo*, was dissolved in benzene, placed on a column of neutral alumina (Woelm) packed wet with hexane, and eluted with 1:1 hexane–benzene. Recrystallization of the solid from hexane gave N-methyl-α,α-dichlorothionacetanilide (3.5 g., 0.015 mole, 60%), m.p. 103°. The infrared spectrum was identical with that of a sample prepared as described previously.

C. From N-Methyl-N-phenyl-1,2,2-trichlorovinylamine.—A solution of N-methyl-N-phenyl-1,2,2-trichlorovinylamine[2] (4.3 g., 0.018 mole) in methylene chloride (50 ml.) was stirred while hydrogen chloride was passed through the solution for 1 min. Hydrogen sulfide was passed through the solution for 2 hr. and the solution was evaporated to dryness *in vacuo*. Recrystallization of the residue from hexane gave N-methyl-α,α-dichlorothionacetanilide (3.3 g., 0.014 mole, 78%), m.p. 103°. The infrared spectrum was identical with that of a sample prepared as described previously.

N,N-Diethyl-α,α-dichlorothionacetamide (VIId).—A solution of N,N-diethyl-1,2,2-trichlorovinylamine (4.0 g., 0.02 mole) in methylene chloride was stirred and saturated with hydrogen chloride. Hydrogen sulfide was passed through the solution for 0.5 hr. and the solution was evaporated to dryness *in vacuo*. The residue was dissolved in pentane and placed on a column of neutral alumina (Woelm) packed wet with pentane. Elution with pentane gave N,N-diethyl-α,α-dichlorothionacetamide as a yellow oil (2.9 g., 0.0145 mole, 73%).

Anal. Calcd. for $C_6H_{11}Cl_2NS$: C, 36.00; H, 5.54; Cl, 35.43; N, 7.00. Found: C, 36.21; H, 5.78; Cl, 35.40; N, 6.76.

N-Methyl-α,α,α-trichlorothionacetanilide (XIIc).—A solution of N-methyl-N-phenyl-1,2,2-trichlorovinylamine (4.3 g., 0.019 mole) in carbon tetrachloride (50 ml.) was stirred at 0° and chlorine was passed into the solution until it became yellow and the temperature ceased to rise. The flow of chlorine was regulated so that the temperature did not exceed 10°. Removal of the carbon tetrachloride, *in vacuo*, left an orange oil. Methylene chloride (50 ml.) was added and hydrogen sulfide was passed through the solution for 0.5 hr. The methylene chloride was removed *in vacuo* and the orange, oily residue was dissolved in pentane and placed on a column of neutral alumina (Woelm) packed wet with pentane. Elution with hexane gave an orange oil which solidified after standing 48 hr. in an open beaker. Recrystallization from hexane gave N-methyl-α,α,α-trichlorothionacetanilide as a yellow solid (3.3 g., 0.012 mole, 63%), m.p. 71–72°.

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[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 356.

[12] The possibility that the two absorptions are due to *syn–anti* isomerism caused by restricted rotation about the C–N bond appears remote since N-methylthionacetanilide shows only one absorption in the 7.5 τ region. The τ-value at which the two absorptions coalesce is not reported because of the difficulty in referencing the Varian A-60 instrument at temperatures above 30°.

[13] Melting and boiling points are uncorrected.

Anal. Calcd. for $C_9H_8Cl_3NS$: C, 40.24; H, 3.00; Cl, 39.60; N, 5.22. Found: C, 40.33; H, 3.14; Cl, 39.59; N, 5.22.

N,N-Diethyl-α,α,α-trichlorothionacetamide (XIId).—A solution of N,N-diethyl-1,2,2-trichlorovinylamine[2] (4.8 g., 0.024 mole) in carbon tetrachloride (40 ml.) was stirred at 0° while chlorine was passed into the solution until it was no longer absorbed. The carbon tetrachloride was removed *in vacuo* and the residue was dissolved in methylene chloride (40 ml.). Hydrogen sulfide was passed through the solution for 1 hr. and the methylene chloride was removed *in vacuo*. The residue was dissolved in pentane and placed on a column of neutral alumina (Woelm) packed wet with pentane. Elution with pentane gave a yellow oil which was redissolved in pentane and placed on a fresh column of alumina. Elution with pentane gave N,N-diethyl-α,α,α-trichlorothionacetamide as a yellow oil (3.1 g., 0.0135 mole, 56%).

Anal. Calcd. for $C_6H_{10}Cl_3NS$: C, 30.72; H, 4.29; Cl, 45.34; N, 5.97. Found: C, 31.01; H, 4.66; Cl, 46.86; N, 5.77.

α,α-Dichlorothionacetanilide (Xb).—A mixture of α,α-dichloroacetanilide (5.1 g., 0.027 mole), phosphorus pentasulfide (2.8 g., 0.0125 mole), and benzene (25 ml.) was refluxed for 1 hr. and filtered. Chilling of the filtrate in an ice bath caused α,α-dichloroacetanilide (3.0 g., 59%) to separate. The filtrate was evaporated *in vacuo* and the residue was extracted with hot hexane. The hexane solution was filtered through charcoal and chilled. This produced α,α-dichlorothionacetanilide as a yellow solid (0.4 g., 0.0018 mole, 18% based on recovered starting material), m.p. 71–72°.

Anal. Calcd. for $C_8H_7Cl_2NS$: C, 43.65; H, 3.21; Cl, 32.21; N, 6.36; S, 14.57. Found: C, 44.36; H, 3.61; Cl, 31.69; N, 6.81; S, 14.11.

Reaction of N-Methyl-α,α,α-trichloroacetanilide and Phosphorus Pentasulfide.—A mixture of N-methyl-α,α,α-trichloroacetanilide (5.0 g., 0.02 mole), phosphorus pentasulfide, (4.4 g., 0.02 mole), and toluene (50 ml.) was refluxed for 16 hr. The toluene was removed *in vacuo* and the residue was extracted with hot benzene. The benzene solution was placed on a column of neutral alumina (Woelm) packed wet with pentane. Elution with benzene gave N-methyl-α,α-dichlorothionacetanilide (0.5 g., 0.002 mole, 10%), m.p. 103°. The infrared spectrum was identical with that of the sample prepared as described previously.

N-Methylthionacetanilide.[14]—N-Methylacetanilide (14.9 g., 0.1 mole) and phosphorus pentasulfide (22.2 g., 0.1 mole) were refluxed in xylene for 17 hr. The solution was decanted from a tarry residue and the xylene was distilled *in vacuo*. The residue was dissolved in benzene and placed on a column of alumina packed wet with hexane. Elution with benzene and recrystallization from benzene–hexane gave N-methylthionacetanilide (4.6 g., 0.028 mole, 28%), m.p. 56–58°.

Anal. Calcd. for $C_9H_{11}NS$: C, 65.40; H, 6.71; N, 8.48; S, 19.40. Found: C, 65.44; H, 7.01; N, 8.14; S, 19.14.

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[14] With Joan E. Fedder.

Pyrolysis Studies. VIII.[1] Polar Substituent Effects in the Vapor Phase Thermal Decomposition of Isopropyl Benzoates

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The absolute reaction rates of thermal decomposition of a series of *meta*- and *para*-substituted isopropyl benzoates have been measured in the vapor phase, using a new pyrolysis apparatus in which the pressure changes were monitored continuously and automatically. Electron-withdrawing substituents were found to increase the rate of decomposition and the relative rates were best correlated by Taft's σ^0-values ($\rho = 0.33$). The σ^0-values for the groups *p-t*-Bu, *p*-Ph, and β-naphthyl were found to be −0.18, +0.08, and +0.15, respectively. Differences between Taft's σ^0-values and Wepster's σ^n-values are discussed, and it is concluded that the Taft σ^0-values give the better measure of the polar effects of *meta* and *para* substituents. The physical properties of eleven new substituted isopropyl benzoates are reported.

For reactions and equilibria involving simple benzene derivatives, it has been fairly generally accepted that the Hammett σ-values derived from the ionization constants of substituted benzoic acids in water at 25° give quantitative measures of the relative polar effects of *meta*- and *para*-substituted phenyl groups.[3,4] However, this ionization is not entirely free from resonance effects as there is direct conjugation between the reaction site and the ring. For example, when the acids bear R^+ *para* substituents there is greater resonance stabilization in the free acid than in the anion, and this lowers the experimentally observed acidity and leads to anomalous σ-values.

Taft[4] and Wepster[5] recently have realized this and have published tables of revised σ-values, designated σ^0 and σ^n, respectively, which give a quantitative measure of the fundamental polar effects of the substituents. However, although both workers used essentially the same approach to the problem, the agreement between the σ^0- and the σ^n-values is not too precise, which is disturbing as it is necessary to have confident knowledge of these fundamental polar effects in order to understand and explain more complicated effects. It was, therefore, decided to evaluate and compare these two sets of polar substituent values by experiment, using data obtained from vapor phase kinetic studies. Measurements were confined to the vapor phase to preclude solvent effects since for some substituents Taft found it necessary to propose *two* σ^0-values, one to be used when dealing with studies in hydroxylic solvents and the other for nonhydroxylic solvents.[4]

Previous studies have shown that the relative rates of vapor phase pyrolysis of *meta*- and *para*-substituted ethyl benzoates to ethylene and the corresponding substituted benzoic acids correlate with Taft's σ^0-values better than with the normal Hammett σ-values.[1] Unfortunately, the σ-value in this reaction was rather small (0.20) and although the relative rates could be measured to within ±3%, this is not sufficiently precise to permit a meaningful comparison of σ^0 and σ^n correla-

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[1] Part VII: G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, **28**, 403 (1963).

[2] Postdoctoral Research Associate, 1961–1962.

[3] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

[4] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

[5] H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).