(2e): C, 69.15; H, 4.93; N, 12.10. Found: C, 69.00; H, 5.03; N, 12.06. Calcd for $C_{14}H_{11}N_5O_2$ (3b): C, 59.78; H, 3.94; N, 24.90. Found: C, 59.56; H, 4.14; N, 24.57.

3-Cyanocoumarinimide (8a) and Its 8-Methoxy Derivative 8b.—To a solution of malononitrile (3.3 g, 0.05 mol) and salicylaldehyde (6.1 g, 0.05 mol) in ethanol (30 ml), ammonium acetate (2.31 g, 0.03 mol) was added and stirred for few minutes. This mixture afforded 5.5 g (65%) of **8a**, mp 162–164° dec (lit.[4] mp 163–165° dec). When 3-methoxysalicylaldehyde was used instead of salicylaldehyde, the condensation afforded 89% **8b**: mp 172–174° dec; ν_{max}^{KBr} 3290 (NH), 2220 (C≡N), 1650 cm^{-1} (C=NH).

Anal. Calcd for $C_{11}H_8N_2O_2$: C, 65.99; H, 4.03; N, 13.99. Found: C, 65.93; H, 3.97; N, 14.20.

Formation of 4-Amino-5-imino-2-phenyl[1]benzopyrano[3,4-*c*]pyridine (2a) by the Reaction of 8a and Acetophenone.—To a mixture of **8a** (0.8 g) and acetophenone (0.72 g) in ethanol (5 ml), ammonium acetate (1 g) was added and heated for 0.5 hr. After cooling, deposited crystals were collected and recrystallized from ethanol–pyridine to give 0.4 g of pale yellow needles (Table II).

Anal. Calcd for $C_{18}H_{13}N_3O$: C, 75.24; H, 4.56; N, 14.63. Found: C, 74.92; H, 4.52; N, 14.87.

Reaction of 2a and Salicylaldehyde.—To a mixture of **2a** (0.2 g) and salicylaldehyde (0.2 g) in ethanol (5 ml), ammonium acetate (0.5 g) was added and heated for 0.5 hr. Yellow-orange crystals precipitated out during the reaction. Recrystallization from pyridine gave 0.2 g of yellow crystals, mp 301–302°. This compound was proved to be identical with **1a** by a study of their ir spectra.

Reaction of 4-Amino-5-imino-7-methoxy-2-phenyl[1]benzopyrano[3,4-*c*]pyridine (2c) and Hydrochloric Acid.—To a mixture of **2c** (0.3 g) and ethanol (7 ml), hydrochloric acid (3 ml) was added and heated for 1 hr. After the mixture cooled, the resulting precipitate was collected and recrystallized from pyridine–ethanol to afford 0.2 g of 4-amino-7-methoxy-5-oxo-2-phenyl[1]benzopyrano[3,4-*c*]pyridine (**7b**): mp 219–220°; ν_{max}^{KBr} 3400, 3280, 3170 (NH_2), 1700 cm^{-1} (C=O).

Anal. Calcd for $C_{19}H_{14}N_2O_3$: C, 71.69; H, 4.43; N, 8.80. Found: C, 71.44; H, 4.61; N, 9.08.

Formation of 2-Aryl-5-methyl[2,3,4-*de*]benzopyrano[2,3-*d*]-pyridopyrimidine (5) by the Reaction of 2 and Acetic Anhydride.—A mixture of **2** (0.7 mmol) and acetic anhydride (4–6 ml) in pyridine (2–4 ml) was heated for 1–2 hr. After the mixture cooled, the resulting precipitate was collected and washed with dilute methanol. Experimental results are summarized in Table III.

Anal. Calcd for $C_{20}H_{13}N_3O$ (**5a**): C, 77.15; H, 4.21; N, 13.50. Found: C, 76.87; H, 4.21; N, 13.48. Calcd for $C_{20}H_{12}N_4O_3$ (**5b**): C, 67.41; H, 3.39; N, 15.72. Found: C, 67.53; H, 3.26; N, 15.75. Calcd for $C_{21}H_{15}N_3O_2$ (**5c**): C, 73.89; H, 4.43; N, 12.31. Found: C, 73.62; H, 4.44; N, 12.40. Calcd for $C_{21}H_{14}N_4O_4$ (**5d**): C, 65.28; H, 3.65; N, 14.50. Found: C, 64.93; H, 3.51; N, 14.28.

Formation of 2-Acetamino-1-cyano-5-methyl[2,3,4-*de*]benzopyrano[2,3-*d*]pyridopyrimidine (6) by the Reaction of 3 and Acetic Anhydride.—To a solution of **3** (0.4 mmol) suspended in pyridine (2 ml), acetic anhydride (2 ml) was added and heated for 1 hr. A pale yellow crystals began to separate from the solution. Experimental results are also listed in Table III.

Anal. Calcd for $C_{17}H_{11}N_5O_2$ (**6a**): C, 64.35; H, 3.49; N, 22.07. Found: C, 64.21; H, 3.57; N, 22.24. Calcd for $C_{18}H_{13}N_5O_3$ (**6b**): C, 62.24; H, 3.78; N, 2 0.17. Found: C, 61.88; H, 3.60; N, 19.89.

Acetylation of 1.—Acetic anhydride (3–6 ml) was added to a solution of **1** (0.2 g) suspended in pyridine (2–3 ml) and refluxed for 2 hr. After the mixture cooled, deposited crystals were collected and recrystallized from pyridine or dimethyl sulfoxide to afford **4** as pale yellow crystals. Experimental results and spectral data (ir and nmr) are summarized in Table I.

Anal. Calcd for $C_{27}H_{17}N_3O_3$ (**4a**): C, 75.17; H, 3.94; N, 9.74. Found: C, 74.89; H, 3.72; N, 9.88. Calcd for $C_{28}H_{19}N_3O_4$ (**4b**): C, 72.87; H, 4.15; N, 9.11. Found: C, 72.63; H, 4.23; N, 8.86. Calcd for $C_{29}H_{19}N_3O_5$ (**4c**): C, 71.16; H, 3.91; N, 8.59. Found: C, 71.13; H, 3.98; N, 8.81. Calcd for $C_{27}H_{16}N_4O_5$ (**4d**): C, 68.06; H, 3.36; N, 11.76. Found: C, 67.87; H, 3.42; N, 11.66. Calcd for $C_{29}H_{21}N_3O_5$ (**4e**): C, 70.87; H, 4.31; N, 8.55. Found: C, 70.92; H, 4.28; N, 8.70.

Registry No.—**1a**, 34035-64-8; **1b**, 34035-65-9; **1c**, 34035-66-0; **1d**, 34035-67-1; **1e**, 34035-68-2; **1f**, 34035-69-3; **1g**, 34035-70-6; **2a**, 30144-15-1; **2b**, 34035-72-8; **2c**, 34035-73-9; **2d**, 34035-74-0; **2e**, 34035-75-1; **3a**, 34035-76-2; **3b**, 34035-77-3; **4a**, 34035-78-4; **4b**, 34035-79-5; **4c**, 34035-80-8; **4d**, 34035-81-9; **4e**, 34087-68-8; **5a**, 34035-82-0; **5b**, 34035-83-1; **5c**, 34035-84-2; **5d**, 34035-85-3; **6a**, 34033-67-5; **6b**, 34033-68-6; **7a**, 34033-69-7; **7b**, 34033-70-0; **8b**, 34033-71-1; malononitrile, 109-77-3; salicylaldehyde, 90-02-8; ammonium acetate, 631-61-8.

Acknowledgment.—The authors wish to express their thanks to Dr. Taro Hayashi and Dr. Tatsuo Takeshima for their kind advice. Thanks are also due to Dr. Haruo Homma and his staff for their microanalyses, to Mr. Jun Uzawa for his measurements of the nmr spectra, and to Mr. Hironori Ogawa for his measurements of the ir spectra.

(4) G. P. Schiemenz, *Chem. Ber.*, **95**, 483 (1962).

Chemistry of α,α-Dichlorosulfenyl Chlorides

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Received September 20, 1971

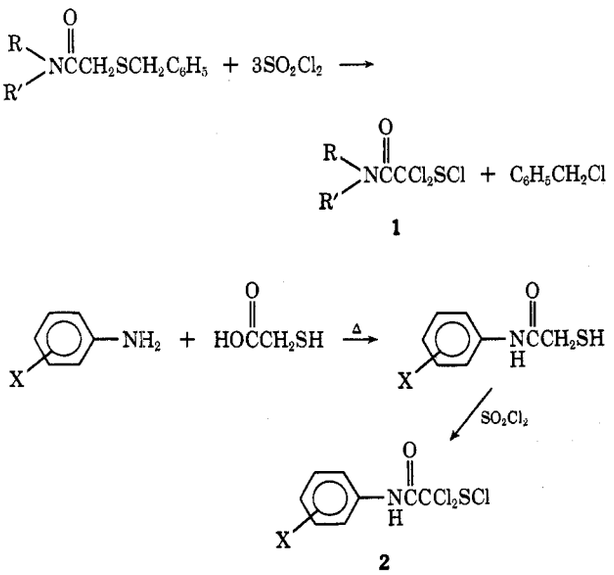
A convenient two-step general synthesis of α(carbamoyl)-α,α-dichloromethyl sulfenyl chlorides is described. These sulfenyl chlorides have been shown to undergo normal displacement of chloride from sulfur upon reaction with primary and secondary amines, alcohols and phenols, sulfinates, *O,O*-diethyldithiophosphoric acid, and phosphites. With liquid ammonia the sulfenyl chlorides yield 1-cyanoformamides. Other characteristic sulfenyl chloride reactions of these compounds include synthesis of (1) 1,2,4-thiadiazoles from amidines, (2) carbonylsulfenyl chlorides upon treatment with sulfuric acid–water, and (3) 2-chloro-2-thioxoacetamides with triphenylphosphine. Ring closure of these sulfenyl chlorides catalyzed by aluminum chloride produces 2-indolinones.

In a recent paper[1] we reported a general synthesis of functionalized α,α-dichlorosulfenyl chlorides (*e.g.*, **1**) *via* chlorination of the appropriate benzyl sulfide.

Presently we wish to report a new route for the synthesis of related compounds (**2**) and our studies of the chemical reactivity of dichlorosulfenyl chlorides (**1**).

Chlorination of α-Mercaptoacetanilides.—Chlorination of α-mercaptoacetanilides has been found to produce α-carbamoyl-α,α-dichlorosulfenyl chlorides (**2**) in good yield. The sequence initially involves simply

(1) W. G. Phillips and K. W. Ratts, *J. Org. Chem.*, **36**, 3145 (1971).

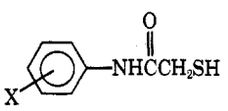


X = 4-Cl, 4-Br, 3-Br, 3-CF_3, 4-OCH_3, 4-CH_3, H, 2,6-di-C_2H_5, 2,6-di-CH_3

heating the appropriate aniline with readily available thioglycolic acid to produce the corresponding α-mercaptoacetanilide. Addition of 3 equiv of sulfuryl chloride to the α-mercaptoacetanilide yields the sulfenyl chloride. The reaction is general in that a variety of substituents on the aniline may be employed (Tables I and II).

TABLE I

α-MERCAPTOACETANILIDES[a]

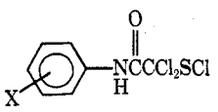


Registry no.	X	Mp, °C	Yield, %
	H	107–110[b]	93
34282-25-2	4-Cl	127–129	20
34282-26-3	3-CF_3	35–40	67
34282-27-4	2,6-Di-C_2H_5	120–124	37
34282-28-5	2,6-Di-CH_3	101–109	55
34282-29-6	4-OCH_3	111–115	90
34282-30-9	4-CH_3	117–123	95

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in the table. [b] Lit. mp 107–110°; W. Pacha and H. Erlenmeyer, *Helv. Chim. Acta*, **135**, 1156 (1956).

TABLE II

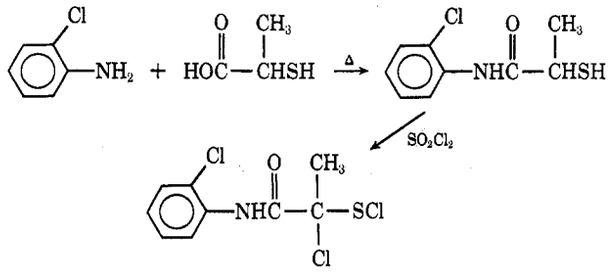
DICHLOROSULFENYL CHLORIDES[a]



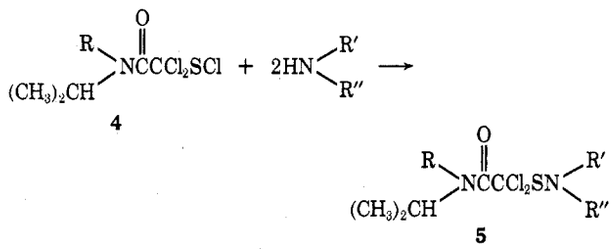
Registry no.	X	Mp, °C	Yield, %
34282-31-0	H	71–76	92
34282-32-1	4-Cl	71–73	40
34282-33-2	3-CF_3	60–62	65
34282-34-3	2,6-Di-C_2H_5	159–162	81
34282-35-4	2,6-Di-CH_3	115–117	50
34282-36-5	4-OCH_3	72–74	27
34282-37-6	4-CH_3	96–97	14

[a] Satisfactory analytical data (±0.4%) were reported for all compounds listed in the table.

A monochlorosulfenyl chloride (**3**) was synthesized simply by substituting α-mercaptopropionic acid for thioglycolic acid.



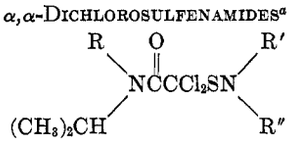
Reaction with N Nucleophiles.—The reaction of dichlorosulfenyl chlorides (**4**) with 2 equiv of a primary or secondary amine yields the dichlorosulfenamide **5**. Some representative examples are shown in Table III.

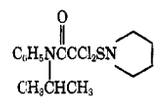
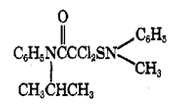
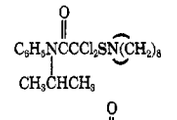
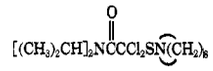
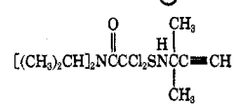
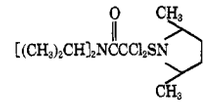


a, R = C_6H_5
b, R = $(CH_3)_2CH$

TABLE III

α,α-DICHLOROSULFENAMIDES[a]

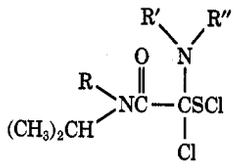


Registry no.	Structure	Mp, °C	Yield, %
34282-38-7		77–79	90
34282-39-8		Oil	
34282-40-1		63–64	30
34282-41-2		116–119	70
34282-55-8		81–83	63
34282-56-9		50–52	59

[a] Satisfactory analytical data (±0.4% for C, H) were reported for all compounds listed in the table.

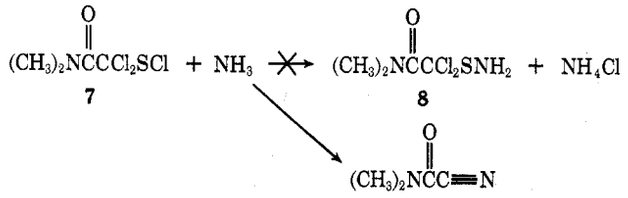
An isomeric sulfenyl chloride structure (**6**) is considered unlikely since trichloromethylsulfenyl chloride has been shown to give sulfenamides with amines.[2]

(2) J. Connolly and G. Dyson, *J. Chem. Soc.*, 679 (1935).



6

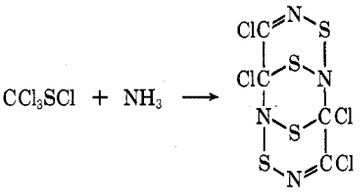
When liquid ammonia is employed as the amine the reaction takes a different course: treatment of **7** with liquid ammonia did not yield the expected sulfenamide **8**. Instead a 10% yield of 1-



7 8

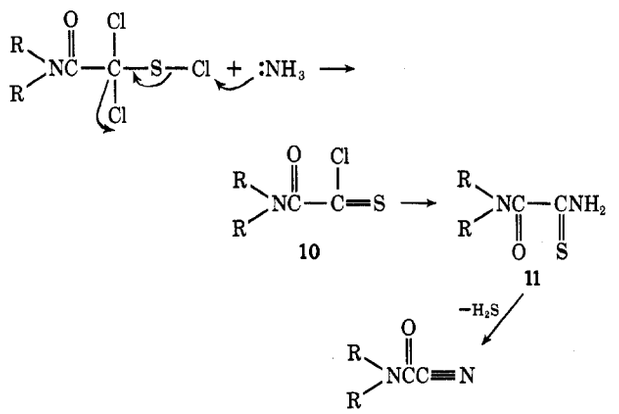
cyano-*N*,*N*-isopropylformamide was obtained. Likewise, when **4b** was treated with liquid ammonia 1-cyano-*N*,*N*-diisopropylformamide was isolated.

In contrast the reaction of trichloromethylsulfenyl chloride in benzene with aqueous ammonia takes a third course. Senning and Kelly reported[3] that **9** is formed in 9% yield under the above conditions. They suggest that trichloromethylsulfenamide is an intermediate in the formation of **9**.



9

A possible mechanism for the formation of the 1-cyanoformamides involves a 2-chloro-2-thioxoacetamide (**10**) as an intermediate, which could form a thioamide (**11**).



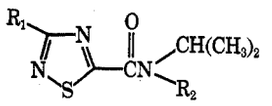
Elimination of hydrogen sulfide from **11** would yield the observed products. That **10** is a likely intermediate was shown when 2-chloro-2-thioxo-*N*,*N*-dimethylacetamide yielded 1-cyano-*N*,*N*-dimethylformamide under the reaction conditions.

The reaction of amides with α-carbamoyl-α,α-dichlorosulfenyl chlorides (**4**) produces 5-carbamoyl-

(3) A. Senning and P. Kelly, *Acta Chem. Scand.*, **20**, 2261 (1966).

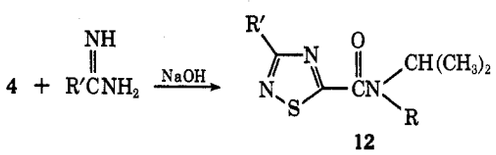
TABLE IV

1,2,4-THIADIAZOLES[a]



Registry no.	R_1	R_2	Mp, °C	Yield, %
34297-85-3		C_6H_5	102–107	20
		$CH(CH_3)_2$	68–72	42
	$4\text{-}ClC_6H_4$	C_6H_5	98–102	13

[a] Satisfactory analytical data (±0.4% for C, H) were reported for all compounds listed in the table.



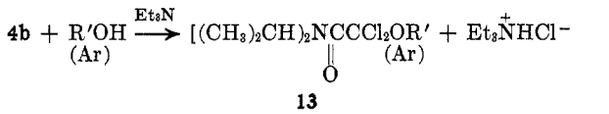
12

a, R = C_6H_5
b, R = $(CH_3)_2CH$

1,2,4-thiadiazoles (**12**) in moderate yield (see Table IV).

Goerdeler, Groschopp, and Sommerlad[4] have reported that amidines and trichloromethylsulfenyl chloride yield 5-chloro-1,2,4-thiadiazoles in a similar manner.

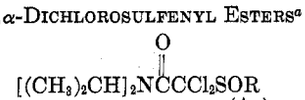
Reaction with O Nucleophiles.—An α,α-dichlorosulfenyl chloride (**4b**) when treated with methanol and substituted phenols in the presence of triethylamine reacts with displacement on sulfur to yield α,α-dichlorosulfenyl esters (**13**). Several representative examples are shown in Table V. In the case of metha-



13

TABLE V

α,α-DICHLOROSULFENYL ESTERS[a]



Registry no.	R	Mp, °C	Yield, %
34282-59-2	CH_3	77–79	90
34297-86-4	$3\text{-}CF_3C_6H_4$	38–40	19
34297-87-5	$3,4,5\text{-Tri-}CH_3C_6H_2$	96–98	69
34282-60-5	$3\text{-}ClC_6H_4$	85–89	72

[a] Satisfactory analytical data (±0.4% for C, H) were reported for all compounds listed in the table.

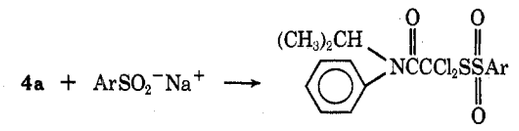
nol, the isomeric sulfoxide structure could be eliminated, since the product gave an nmr absorption at τ 6.5, the region expected for a methoxyl group.[5] A sulfoxide methyl group would be expected to appear at higher field (*e.g.*, DMSO absorbs at τ 7.4[5]). In the case of substituted phenols, reaction with the aromatic

(4) J. Goerdeler, H. Groschopp, and V. Sommerlad, *Chem. Ber.*, **90**, 182 (1957).

(5) Varian NMR Spectra Catalogs.

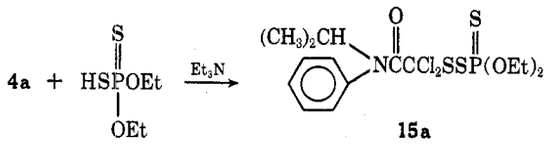
nucleus was precluded by integration of the relative areas of the absorptions in their nmr spectra.

Reaction with S Nucleophiles.—The reaction of an α,α-dichlorosulfenyl chloride (**4a**) with sodium arylsulfonates and *O,O*-diethyldithiophosphoric acid each proceeded *via* displacement on sulfur to yield α,α-dichlorothiolsulfonates (**14**) and a thioperoxyphosphoryldithioate (**15**), respectively.



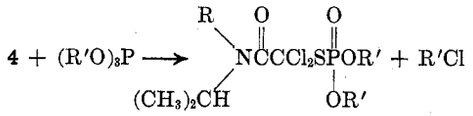
14

a, Ar = C_6H_5
b, Ar = *p*-$CH_3C_6H_4$



15a

Reaction with P Nucleophiles.—With trialkyl phosphites, α,α-dichlorosulfenyl chlorides (**4**) were found to give *S*-dichlorocarbamoylmethyl *O,O*-dialkylphosphorothioates (**16**). Apparently nucleophilic displacement occurs on sulfur followed by an Arbuzov reaction (see Table VI).[6]

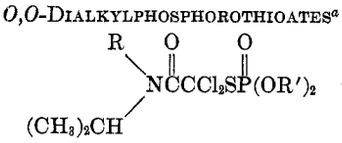


16

a, R = C_6H_5
b, R = $(CH_3)_2CH$

TABLE VI

S-DICHLOROCARBAMOYLMETHYL *O,O*-DIALKYLPHOSPHOROTHIOATES[a]



Registry no.	R	R′	Mp, °C	Yield, %
34282-61-6	C_6H_5	CH_3	91–92	34
34282-62-7	C_6H_5	CH_2CH_3	53–55	91
34282-63-8	$CH(CH_3)_2$	CH_3	129–131	93
34282-64-9	$CH(CH_3)_2$	CH_2CH_3	76–78	25
34282-65-0	$CH(CH_3)_2$	$CH(CH_3)_2$	83–87	70

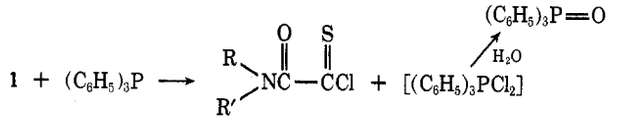
[a] Satisfactory analytical data (±0.4% for C, H, or Cl, S) were reported for all compounds listed in the table.

Dialkyl phosphites more slowly undergo the same reaction with the loss of hydrogen chloride to produce the same products.

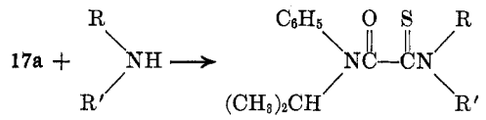
The carbamoyl dichlorosulfenyl chlorides (**1**) upon treatment with triphenylphosphine yield a salt (presumably triphenylphosphonium dichloride) and 2-chloro-2-thioxoacetamides (**17**).

Addition of chlorine to **17a** regenerated the starting sulfenyl chloride.

Treatment of the 2-chloro-2-thioxoacetamide **17a** with various amines yielded the corresponding monothiooxamides (**18**) (see Table VII).

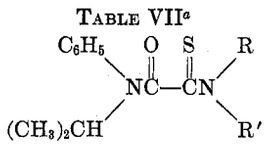


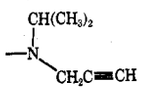
17a, R = C_6H_5; R′ = $(CH_3)_2CH$
b, R = $(CH_3)_2CH$; R′ = $(CH_3)_2CH$
c, R = CH_3; R′ = CH_3



18

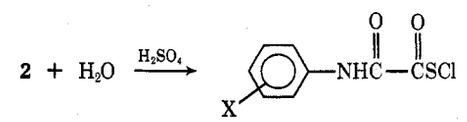
TABLE VII[a]



Registry no.	NRR′	Mp, °C	Yield, %
34282-66-1		108–109	91
34282-67-2		113–115	77
34282-68-3		131–132	99

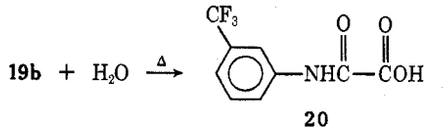
[a] Satisfactory analytical data (±0.4% for C, H) were reported for all compounds listed in the table.

Acid Hydrolysis.—Strong acid hydrolysis of α-carbamoyl-α,α-dichlorosulfenyl chlorides (**2**) yields carbamoylcarbonylsulfenyl chlorides (**19**). The reaction



19a, X = 4-Cl
b, X = 3-CF_3
c, X = 3-Br

appears somewhat general and proceeds in good yields. In one instance, when no care was exercised to keep the reaction temperature cool, a considerable amount of a carboxylic acid **20** was formed. Presumably this was formed *via* hydrolysis of **19b**.



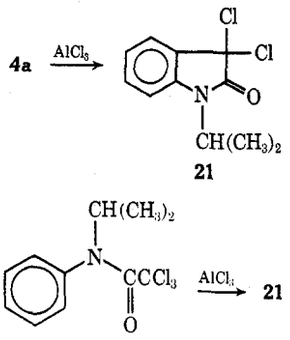
20

Trichloromethylsulfenyl chloride has been shown to undergo an analogous reaction to yield chlorocarbonylsulfenyl chloride.[7]

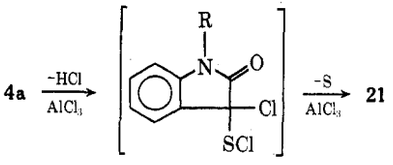
Aluminum Chloride Cyclization.—Treatment of **4a** with aluminum chloride produces 3,3-dichloro-1-isopropyl-2-indolinone (**21**). 3,3-Dichloro-1-isopropyl-2-indolinone was prepared authentically from ring closure of *N*-isopropyl-2,2,2-trichloroacetanilide.

(6) The occurrence of the Arbuzov reaction with phosphites and sulfenyl chlorides has been reported. See P. Asinger, M. Thiel, and W. Schafer, *Justus Liebigs Ann. Chem.*, **637**, 146 (1960).

(7) W. Weiss, German Patent 1,224,720 (Nov. 11, 1964); (Farbenfabriken Bayer A. G).



The product **21** is likely formed as follows.



The catalytic influence of aluminum chloride is known[8] to convert trichloromethanesulfenyl chloride to carbon tetrachloride with loss of sulfur.

Experimental Section

General.—Melting points were determined with a Mel-Temp apparatus and are uncorrected. Infrared spectra were measured with a Beckman IR-5A spectrometer. Nuclear magnetic spectra were obtained on a Varian A-60 or T-60 spectrometer. Synthetic procedures for sulfenyl chlorides not described below are given in an earlier paper.[1]

General Procedure for Preparation of α-Mercaptoacetanilides.—To 92 g (0.95 mol) of 95% thioglycolic acid was added 1.0 mol of the appropriate aniline followed by heating at 130° for 3 hr under nitrogen. The mixture was poured into *ca.* 200 ml of 10% hydrochloric acid, whereupon it crystallized and was collected and air dried overnight. Chloroform proved to be a general recrystallizing solvent, although the resulting crude solid could be used directly in the chlorination step (see Table I).

General Procedure for the Preparation of α,α-Dichlorosulfenyl Chlorides (2).—To 0.1 mol of the appropriate α-mercaptoacetanilide in *ca.* 300 ml of methylene chloride was added 0.3 mol of sulfuryl chloride dropwise (exothermic). After the addition the mixture was stirred for an additional 1 hr. The solvent was then removed and the resulting mass was recrystallized from petroleum ether (bp 30–75°). No effort was made to optimize the yields (see Table II).

o-Chloro-α-mercapto-α-methylacetanilide.—To 53 g (0.5 mol) of α-mercaptopropionic acid was added 65 g (0.5 mol) of *o*-chloroaniline. After heating at 130° for 3 hr, the solution was poured into *ca.* 500 ml of 10% hydrochloric acid and the solid was collected and air dried, yield 26% after recrystallization from chloroform, mp 83–90°.

Anal. Calcd for $C_9H_{10}ClNOS$: C, 50.11; H, 4.67; N, 6.49. Found: C, 50.19; H, 4.86; N, 6.35.

2-(Chlorothio)2,2′-dichloropropionanilide (3).—The general procedure for chlorination of α-mercaptoacetanilides was followed employing *o*-chloro-α-mercaptopropionanilide. The oil was purified by low-temperature recrystallization from petroleum ether, yield 65%.

Anal. Calcd for $C_9H_8Cl_3NOS$: C, 37.98; H, 2.83; N, 4.92. Found: C, 38.03; H, 2.94; N, 4.76.

Treatment of 2-Chloro-2-thioxo-*N*-isopropylacetanilide with Chlorine.—Chlorine was bubbled through a solution of 1.5 g (6.2 mmol) of **17a** in 100 ml of methylene chloride until the red color was discharged. Removal of solvent gave **4a**, which was washed with pentane, yield 1.6 g (83%), mp 121–123° (lit.[1] mp 121–122°).

General Procedure for Preparation of α,α-Dichlorosulfenamides.—To 20 mmol of the sulfenyl chloride in *ca.* 100 ml of benzene was added 40 mmol of the appropriate amine. A precipitate formed immediately, after which the solution was stirred for *ca.* 1 hr. After filtration the solvent was removed and the crude product was recrystallized from petroleum ether (see Table III).

1-Cyano-*N*,*N*-diisopropylformamide.—Into *ca.* 50 ml of ammonia condensed in a three-neck flask was slowly poured 15.0 g of **4b**. Cooling was maintained by a Dry Ice bath for 1 hr, after which the ammonia was allowed to evaporate slowly. The gum which remained was extracted with petroleum ether. Cooling of the petroleum ether in Dry Ice gave a solid which was purified by distilling through a short-path column at low pressure, nmr ($CDCl_3$) τ 5.6 [heptet (h), CH], 6.3 (h, CH), 8.7 (q, CH_3).

Anal. Calcd for $C_8H_{14}N_2O$: C, 62.31; H, 9.15. Found: C, 62.25; H, 9.26.

1-Cyano-*N*,*N*-dimethylformamide.—A procedure analogous to that above was followed. The crude product was distilled at 55° (2 mm), yield 10%, nmr ($CDCl_3$) τ 6.85 (d, CH_3).

Anal. Calcd for $C_4H_6N_2O$: C, 48.97; H, 6.16. Found: C, 48.85; H, 6.21.

Treatment of 2-Chloro-2-thioxo-*N*,*N*-dimethylacetamide (10, R = CH_3) with Liquid Ammonia.—This procedure was analogous to that for the prepartion of 1-cyanoformamides. The product was distilled at reduced pressure, yield 0.5 g (9%). The ir of the product was the same as that of 1-cyano-*N*,*N*-dimethylformamide.

General Procedure for Preparation of Thiadiazoles (12).—The procedure of Goerdeler, Groschopp, and Sommerlad[4] for trichloromethylsulfenyl chloride was followed. Extraction of the crude oil with hot petrpleum ether followed by cooling yielded the pure product (see Table IV). No attempt was made to optimize the yields.

General Procedure for Preparation of α,α-Dichlorosulfenyl Esters.—To 20 mmol of the appropriate sulfenyl chloride in *ca.* 100 ml of benzene was added 20 mmol of the appropriate alcohol (or phenol) followed by 20 mmol of triethylamine. A precipitate formed immediately and the reaction was stirred for *ca.* 30 min. After filtration, the solvent was removed and the crude product was recrystallized from petroleum ether (see Table V).

α,α-Dichloro-α-mercapto-*N*-isopropylacetanilide, *p*-Toluenethiolsulfonate (14b).—To 20 g (excess) of sodium *p*-toluenesulfinate in 100 ml of water was added a carbon tetrachloride solution of 15.6 g (0.05 mol) of **4a**. After stirring overnight, the layers were separated. Removal of the carbon tetrachloride gave a solid: mp 98–100°; nmr ($CDCl_3$) τ 2.4 (Ar, m), 7.55 ($ArCH_3$, s), 8.9 (CH_3, d).

Anal. Calcd for $C_{18}H_{19}Cl_2NO_3S_2$: C, 50.00; H, 4.43. Found: C,-50.05; H, 4.39.

α,α-Dichloro-α-mercapto-*N*-isopropylacetanilide Phenylthiolsulfonate (14a).—The same procedure as that above was followed: mp 86–90° (washed with petroleum ether); yield 71%; nmr ($CDCl_3$) τ 2.3 (Ar, m), 5.1 (CH, h), 8.9 (CH_3, d).

Anal. Calcd for $C_{17}H_{17}Cl_2NO_3S_2$: C, 48.80; H, 4.10. Found: C, 48.88; H, 4.18.

***S*,*S*-Dichloro(diisopropylcarbamoyl)methyl *O*,*O*-Diethylthioperoxyphosphoryldithioate (15b).**—To 3.8 g (20 mmol) of **4b** in benzene was added 5.6 g (20 mmol) of *O*,*O*-diethyldithiophosphoric acid followed by 2.0 g (20 mmol) of triethylamine. After stirring for 1 hr, the solution was filtered and the solvent was removed. The product was recrystallized from petroleum ether, mp 60–63°, yield 5.4 g (64%).

Anal. Calcd for $C_{12}H_{24}Cl_2NO_3PS_3$: C, 33.64; H, 5.65. Found: C, 33.68; H, 5.68.

General Procedure for the Preparation of *S*-Dichlorocarbamoylmethyl *O*,*O*-Dialkylphosphorothioates (16).—To 1 equiv of the sulfenyl chloride in benzene (or methylene chloride) was added 1 equiv of the trialkyl phosphite. After stirring for *ca.* 1 hr, the solvent was removed and the solid was recrystallized from petroleum ether (see Table VI).

2-Chloro-2-thioxo-*N*-isopropylacetanilide (17a).—To 6.2 g (0.02 mol) of α,α-dichloro-α-chlorothiol-*N*-isopropylacetanilide in *ca.* 100 ml of benzene was added 5.2 g (0.02 mol) of triphenylphosphine. After stirring for *ca.* 1 hr, the solvent was removed and a red oil remained. Addition of ether (with cooling) gave a gummy solid which gave off HCl when collected. Addition of water to this gummy solid gave a 97% yield of triphenylphosphine oxide, mp 144–147° (lit.[9] mp 153–156°). The nmr showed only aromatic protons.

(8) F. Boberg, *Justus Liebigs. Ann. Chem.*, **679**, 109 (1964).

(9) "Handbook of Chemistry and Physics," 37th ed, Chemical Rubber Publishing Co., Cleveland, Ohio.

The ether solution was evaporated and an oil remained. Addition of petroleum ether to the oil followed by filtration and cooling to −70° gave an orange solid: mp 35–37°; yield 73%; nmr ($CDCl_3$) τ 2.6 (m, aromatic), 5.1 (h, methane), 8.8 (d, methyl); mass spectrum *m/e* 241 (M^+), 206 (M − HCl), 162 [M − C(=S)Cl], 120 (PhNHC=O), 79 (ClC=S), 77 (Ph).

Anal. Calcd for $C_{11}H_{12}ClNOS$: C, 54.65; H, 5.00. Found: C, 54.80; H, 5.12.

2-Chloro-2-thioxo-*N*,*N*-diisopropylacetamide (17b).—This procedure was identical with that for **17a**: mp 60–63° (petroleum ether); yield 27%; nmr ($CDCl_3$) τ 6.0 (h, 1), 6.5 (h, 1), 8.55 (d, 6), 8.75 (d, 6).

Anal. Calcd for $C_8H_{14}ClNOS$: C, 46.26; H, 6.79; N, 6.74. Found: C, 46.02; H, 6.73; N, 6.62.

2-Chloro-2-thioxo-*N*,*N*-dimethylacetamide (17c).—To 13.2 g (0.061 mol) of α-(*N*,*N*-dimethylcarbamoyl)-α,α-dichloromethylsulfenyl chloride in *ca.* 250 ml of benzene was added 16.0 g (0.061 mol) of triphenylphosphine. After stirring for 1 hr, the solvent was stripped and the product was distilled at reduced pressure, nmr ($CDCl_3$) τ 6.95 (d), yield 67%.

Anal. Calcd for C_4H_6ClNOS: C, 31.69; H, 3.99. Found: C, 32.11; H, 4.04.

General Procedure for the Preparation of Monothiooxamides (18).—To 20 mmol of 2-chloro-2-thioxo-*N*-isopropylacetanilide in *ca.* 100 ml of benzene was added 40 mmol of the appropriate amine. After stirring for *ca.* 1 hr, the precipitate was filtered off and the solvent was removed. The product was recrystallized from petroleum ether (see Table VII).

***p*-Chlorophenylcarbamoylcarbonylsulfenyl Chloride (19a).**—To 6.1 g (0.02 mol) of α,α-dichloro-α-(*p*-chlorophenylcarbamoyl)-methylsulfenyl chloride was added *ca.* 75 ml of concentrated sulfuric acid. After stirring for *ca.* 10 min, the mixture was poured onto ice and the precipitate was collected and air dried, yield 94%. After recrystallization from chloroform the yield was 50%: mp 172–174°; ir ($CHCl_3$) 5.83, 5.90 cm^{-1} (C=O, C=O); nmr (DMSO-d_6) τ 2.3 (q, aromatic).

Anal. Calcd for $C_8H_5Cl_2NO_2S$: C, 38.42; H, 2.02; N, 5.60. Found: C, 38.23; H, 1.94; N, 5.57.

***m*-Trifluoromethylphenylcarbamoylcarbonylsulfenyl Chloride (19b).**—This procedure was analogous to that for **19a**, yield 90%, mp 108–114° (chloroform).

Anal. Calcd for $C_9H_5ClF_3NO_2S$: C, 38.11; H, 1.78; N, 4.94. Found: C, 38.32; H, 1.80; N, 4.86.

When the reaction was repeated on a 125-g scale an attempt was made to recrystallize the product from benzene. A white solid precipitated out which was identified as **20**: yield 25 g; mp 170–171°; mass spectrum *m/e* 233 (M^+), mol wt (benzene) 234 (calcd 233).

Anal. Calcd for $C_9H_6F_3NO_3$: C, 46.36; H, 2.57; N, 6.01. Found: C, 46.52; H, 2.65; N, 6.08.

3-Bromophenylcarbamoylcarbonylsulfenyl Chloride (19c).—This procedure was analogous to that for **19a**, yield 25%, mp 157–161° (chloroform).

Anal. Calcd for $C_8H_5BrClNO_2S$: C, 32.62; H, 1.71; N, 4.76. Found: C, 32.63; H, 1.76; N, 4.73.

$AlCl_3$-Catalyzed Ring Closures. A. From Sulfenyl Chloride.—*N*-Isopropyl *N*-phenylcarbamoyldichloromethylsulfenyl chloride (31.0 g, 0.1 mol) was dissolved in 200 ml of methylene chloride and cooled in an ice bath. Aluminum chloride (26.6 g, 0.2 mol) was added in small portions with stirring over 10 min. After 5 min of additional stirring the red solution was poured onto 500 ml of ice. The organic layer was separated and the aqueous phase was washed with 290 ml of methylene chloride. The combined organic layers were dried over magnesium sulfate and concentrated to an oil. Addition of hot petroleum ether (bp 30–75°) crystallized 4.8 g of 3,3-dichloro-1-isopropyl-2-indolinone (**21**). Concentration of the filtrate gave a gummy solid which was recrystallized from methylene chloride–petroleum ether to give an additional 5.0 g of solid for which the nmr was identical with that of the original solid, total yield 9.8 g (25%). Recrystallization of the product (4.8 g) from petroleum ether gave 3.7 g of **21**, mp 78–79°.

Anal. Calcd for $C_{11}H_{11}Cl_2NO$: C, 54.12; H, 4.54; Cl, 29.05; N, 5.74. Found: C, 54.19, 54.14; H, 4.62, 4.65; Cl, 28.47, 28.48; N, 5.81, 5.62.

The nmr spectrum ($CDCl_3$) exhibits peaks for CH_3 at τ 8.53 (d, J = 7 cps, A = 6), CH at 5.57 (septet, J = 7 cps, A = 1), ArH at 2.2–3.1 (multiplet, A = 4). The ir spectrum ($CHCl_3$) exhibits a single peak for C=O at 1730 cm^{-1}. Mass spectral characteristics are *m/e* 243 (44%, M^+ for ^{35}Cl), 228 (14%, M − CH_3), 208 (90%, M − Cl), 200 (27%, M − C_3H_7), 166 (100%, M − C_3H_6Cl).

B. From Trichloroacetanilide.—*N*-Isopropyl-2,2,2-trichloroacetanilide (2.8 g, 0.01 mol) was dissolved in 20 ml of methylene chloride, and aluminum chloride (2.7 g, 0.02 mol) was added in portions. After stirring overnight the mixture was poured onto ice (400 ml) and the layers were separated. The aqueous layer was washed with two 50-ml portions of methylene chloride and the combined organic layers were dried over magnesium sulfate. Removal of solvent gave an oil which was crystallized from petroleum ether to give 0.6 g (25%) of product identical with the above material **21**.

***N*-Isopropyl-2,2,2-trichloroacetanilide.**—*N*-Isopropylaniline (135.2 g, 1.0 mol) was dissolved in 250 ml of benzene, and trichloroacetyl chloride (181.1 g, 1.0 mol) was added slowly with stirring. Triethylamine (101.2 g, 1.0 mol) was added dropwise with vigorous stirring to the boiling mixture over 30 min. The mixture was filtered, the filter cake was washed with benzene, and the combined organic filtrate was washed twice with 10% hydrochloric acid (250 ml). The benzene solution was washed twice with 250 ml of water and dried over magnesium sulfate. Removal of the benzene *in vacuo* gave an oil which was crystallized from methanol to give 101.3 g (36%) of product, mp 45–47°.

Registry No.—**3**, 34282-69-4; **14a**, 34282-70-7; **14b**, 34282-71-8; **15**, 34282-72-9; **17a**, 34282-73-0; **17b**, 34282-74-1; **17c**, 34282-75-2; **19a**, 34282-76-3; **19b**, 34282-77-4; **19c**, 34282-78-5; **20**, 6890-83-1; **21**, 34282-79-6; *O*-chloro-α-mercapto-α-methylacetanilide, 34282-80-9; 1-cyano-*N*,*N*-diisopropylformamide, 34282-81-0; 1-cyano-*N*,*N*-dimethylformamide, 16703-51-8; *N*-isopropyl-2,2,2-trichloroacetanilide, 34282-83-2.