

Other pertinent crystallographic data and parameters may be found in the microfilm edition.²¹

Registry No.—3b, 36146-94-8; 4, 36146-93-7; 6a, 29376-74-7; 6b, 36146-96-0; 11a, 36146-97-1; 11b,

(21) The observed and calculated structure factors, atomic coordinates, and temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-3810. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

36146-98-2; 12, 35133-13-2; 13, 36147-00-9; 15, 23210-25-5; 16, 36147-01-0; 17, 10572-61-9; 18, 36147-03-2; 19, 36147-04-3; 23a, 36138-85-9; 23c, 36138-86-0; 24b, 36147-05-4; 24e, 36147-06-5; 25a, 36138-87-1; 25b, 1611-83-2; 25c, 36138-88-2; 25d, 6554-73-0; 25e, 32119-42-9; 25f, 36147-10-1; 26b, 4406-41-1; 26c, 36146-78-8; 26d, 7472-49-3; 26e, 2719-26-8; 27a, 36146-81-3; 28, 19155-24-9; 31, 13616-67-6; phenylethylketene, 20452-67-9.

Carbamoyl Chlorosulfines

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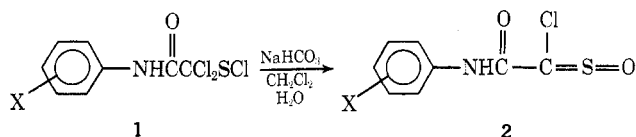
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The synthesis of novel carbamoyl chlorosulfines *via* two different pathways is described. In some cases these reagents slowly convert to a geometrical isomer at room temperature. An assignment of structure to the geometrical isomers is proposed on the basis of physical and spectra data. These sulfines yield α -chloroacetamides upon strong base hydrolysis.

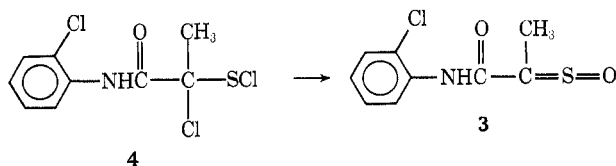
In previous papers we reported that carbamoyldichlorosulfonyl chlorides can be conveniently synthesized^{1,2} and that these substances undergo a wide range of reactions.² We now wish to report that mild basic hydrolysis of these reagents conveniently yields novel carbamoylchlorosulfines in moderate yield.

Treatment of 1 with aqueous sodium bicarbonate in a two-phase system employing methylene dichloride as a cosolvent yields carbamoyl chlorosulfines (2) in



- 1
2
- a, X = 4-Cl
b, X = 3-CF₃
c, X = 3-Br
d, X = 4-OCH₃
e, X = 4-CH₃
f, X = 2,6-di-CH₃
g, X = 2-CH₃, 6-*t*-C₄H₉

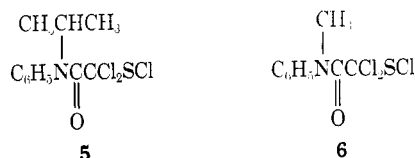
24–57% yield after purification. The reaction is general in that a variety of aromatic substituents may be employed. Water may be substituted for the aqueous bicarbonate although the reaction appears to be slower. In one instance a carbamoyl alkyl sulfine (3) was prepared in low yield by hydrolysis of the corresponding sulfonyl chloride (4). The only previous



example of the preparation of a sulfine *via* hydrolysis of a sulfonyl chloride is that of Silhanek and Zbirovsky³ who reported that dichloromethylene sulfoxide may be

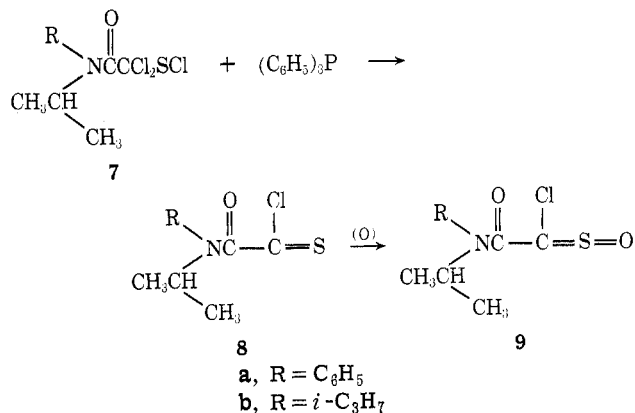
prepared by hydrolysis of trichloromethanesulfonyl chloride.

The sequence is not applicable to *N,N*-disubstituted carbamoyl sulfonyl chlorides. Treatment of 5 with aqueous sodium bicarbonate for 3 days resulted in a high recovery of starting material while 6 slowly yielded



a mixture of unidentified products from which no sulfine could be isolated.⁴

N,N-Disubstituted carbamoyl chlorosulfines may be prepared by another route. Treatment of *N,N*-disubstituted carbamoyldichlorosulfonyl chlorides (7) with triphenylphosphine yields the corresponding 2-chloro-2-thioxo-*N,N*-(disubstituted)acetamide (8).² Oxidation of these substances with *m*-chloroperbenzoic acid yields the sulfines in moderate yield.



In some cases the sulfines formed *via* the hydrolysis route were thermodynamically unstable. For ex-

(4) Attempts to extend this synthetic route to other sulfonyl chlorides failed; hydrolysis of phenylsulfonyldichloromethylsulfonyl chloride with weak base yielded no reaction while hydrolysis of cyanodichloromethylsulfonyl chloride yielded α -chloroacetone nitrile.

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

(2) W. G. Phillips and K. W. Ratts, *ibid.*, **37**, 1526 (1972).

(3) J. Silhanek and M. Zbirovsky, *Chem. Commun.*, 878 (1969).

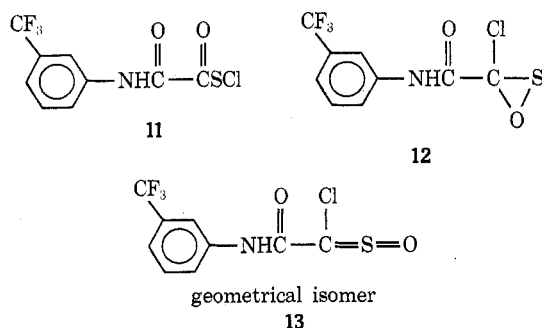
ample, **2b** was found to rearrange to a monomeric isomer **10** with a half-life of about 1 week at room temperature. The reaction was easily followed by observing the disappearance of the strong band at 1015 cm^{-1} in the infrared spectrum of **2b**.

The infrared and ultraviolet spectral data for the two isomers are shown in Table I. The carbonyl

TABLE I
SPECTRAL DATA FOR **2b** AND **10**

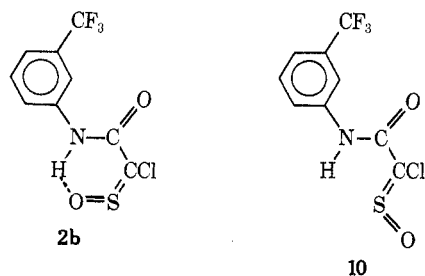
	2b	10
Ir (CDCl ₃), cm ⁻¹	1695 (C=O) 3360 (N-H) 1015	1670 (C=O) 3445 (N-H) No band at 1015
UV (CH ₃ CN), mμ (ε)	τ _{max} 228 (6488), 288 (4384)	τ _{max} 230 (6422), 302 (6922)

frequency suggested that the isomer must be **11**, **12**, or **13**.^{5,6}



The sulfenyl chloride **11** could be ruled out by comparison with an authentic sample.² The ultraviolet spectrum of **10** eliminates **12** from consideration; **12** would not be expected to have a band at $302\text{ m}\mu$. Thus one can conclude that **2b** slowly converts to a geometrical isomer.

Information suggesting an assignment of configuration has been obtained. An examination of models of the two geometrical isomers suggests that intramolecular hydrogen bonding can readily occur in one of the configurations. Since **2b** is considerably more volatile than **10**,⁷ this suggests that **2b** and **10** have the configurations shown below. Their infrared spectra



also support this conclusion. The N-H frequency of **2b** is lower than that of **10** and is in the range for a hydrogen bonded N-H.⁸ Also **2b** would be expected

(5) The bent nature of the C=S=O group is well established, King and Durst⁶ have succeeded in isolating the two isomers oxythiobenzoyl chlorides by fractional crystallization and proposed assignment of configurations on the basis of dipole moment.

(6) J. F. King and T. Durst, *J. Amer. Chem. Soc.*, **85**, 2676 (1963).

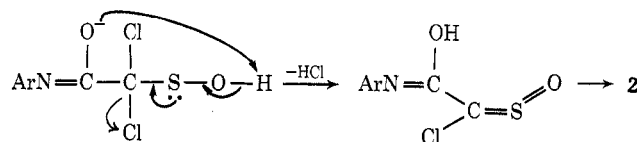
(7) Compound **2b** volatilizes into the mass spectrograph at 40° while **10** does not produce an ion current until 220° is reached.

(8) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 207.

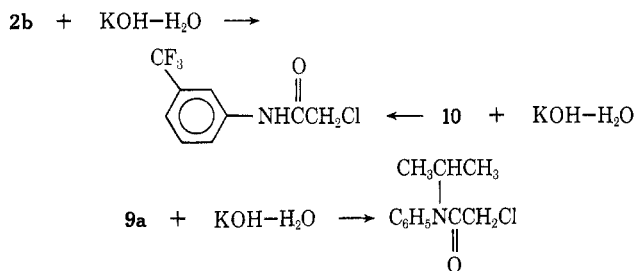
to have a higher carbonyl frequency than **10** since its carbonyl is forced to become coplanar with a chlorine atom.

Analogously **2d** also was found to undergo an isomerization upon heating. A higher melting compound (**14**) was formed which had a higher N-H band and a lower carbonyl band in its infrared spectrum.

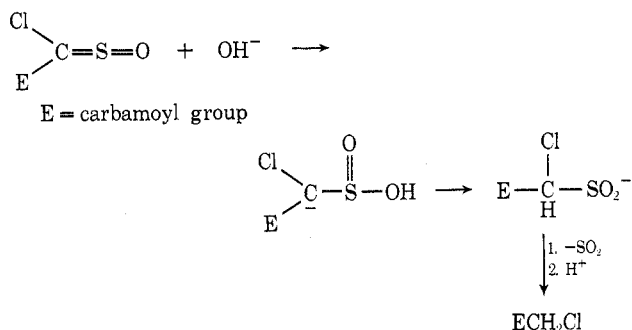
The mechanism of the mild basic hydrolysis of α , α -dichlorosulfonyl chlorides is not known. However, it is tempting to speculate that a sulfenic acid is first formed which loses hydrogen chloride *via* an internal base. This would account for the observed stereochemistry of the initial sulfine.



The carbamoyl chlorosulfines have been found to yield α -chloroacetanilides in good yield upon treatment with strong base. A likely mechanism involves Michael addition of hydroxide ion to the sulfine to

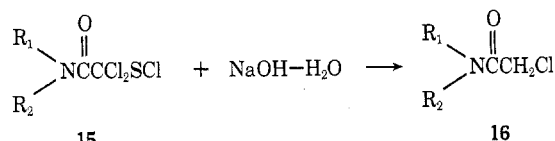


yield a sulfenic acid which can lose sulfur dioxide to yield α -chloroacetanilide. The only previous example of a Michael addition to a sulfine is that of Schultz



and Schlessinger⁹ who found that treatment of diaryl-sulfines with methyllithium gave methyl sulfoxides.

Direct strong basic hydrolysis of the carbamoyl-dichloromethylsulfonyl chlorides also yields α -chloroacetanilides. Presumably a carbamoyl chlorosulfine is an intermediate in these reactions.



a, R₁ = C₆H₅; R₂ = *i*-C₃H₇

b, R₁ = *i*-C₃H₇; R₂ = H

c, R₁ = H; R₂ = 2-CH₃-6-*t*-C₄H₉C₆H₃

d, R₁ = 2,6-(C₂H₅)₂C₆H₃; R₂ = CH₂OCH₃

(9) A. G. Schultz and R. H. Schlessinger, *Chem. Commun.*, 747 (1970).

Experimental Section

Melting points are uncorrected. Infrared spectra as chloroform solutions were determined on a Beckman IR-5A instrument. Nmr spectra were determined on a Varian A-60 or T-60 instrument. Procedures for the preparation of the sulfonyl chlorides are described in our earlier papers.^{1,2}

General Procedure for Preparation of Carbamoyl Chlorosulfines via Hydrolysis Route (Method A).—To one part by weight of the appropriate α,α -dichlorosulfonyl chloride in methylene chloride was added one part of sodium bicarbonate in water. The volumes of methylene chloride and of water were approximately equal. After stirring vigorously *ca.* 0.5 hr, the layers were separated; the organic layer was dried (MgSO_4). Removal of the solvent gave a mass which was triturated with a small amount of ether. Collection of the solid generally gave a pure product although the product could usually be recrystallized from petroleum ether (bp 30–75°) (see Table II).

TABLE II
CARBAMOYL CHLOROSULFINES^a

No.	Mp, °C	Yield, %	Synthesis method
2a	111–113	49	A
2b	89–91 ^b	57	A
2c	110–111	52	A
2d	98 ^c	50	A
2e	95–98	26	A
2f	101–109	52	A
2g	168–169	42	A
3	103–105	8	A
9a	48–55 ^d	19	B
9b	47–51	79	B
10 ^e	139–140	50	...
14 ^f	143–145	80	...

^a Satisfactory analytical values ($\pm 0.25\%$ for C, H, and N) were reported for all compounds. ^b This product melts at 89–91° and resolidifies and melts again at *ca.* 120°. The mass spectrum showed a molecular ion at 283 and a base peak at 235 ($\text{M}^+ - \text{SO}$). The molecular weight in benzene was 333 (calcd 284). ^c This product melts at 98° and resolidifies and melts again at 137–140°. ^d Mass spectra data: 267 (M^+); 209 ($\text{M}^+ - \text{SO}$, base peak). ^e Prepared by heating 2b on a steam bath for 0.5 hr; the molecular weight in benzene was 293 (calcd 284). ^f Prepared by heating 2d on a steam bath for 0.5 hr.

Preparation of Carbamoyl Chlorosulfines via Oxidation of the Corresponding 2-Chloro-2-thioxoacetamide (Method B).—To 1 equiv of the 2-chloro-2-thioxoacetamide² in methylene chloride was added 0.95 equiv of *m*-chloroperbenzoic acid (exothermic). The red color was immediately discharged. After 0.5 hr of stirring the *m*-chlorobenzoic acid was filtered and the resulting solution extracted with a cold, dilute, aqueous sodium bicarbonate solution. Removal of the solvent gave an oil which was

taken up in pentane. Cooling of the pentane solution in Dry Ice gave a solid (see Table II).

Attempted Hydrolysis of α -(*N*-Phenyl-*N*-isopropylcarbamoyl)- α,α -dichloromethylsulfonyl Chloride.—The general procedure of sodium bicarbonate hydrolysis of α,α -dichlorosulfonyl chlorides was followed except that a reaction time of 3 days was employed. The recovery of starting material was 90%, mp 121–123° (lit.¹ mp 121–122°). Its ir spectrum was identical with that of 5.

Attempted Hydrolysis of α -Phenylsulfonyl- α,α -dichloromethylsulfonyl Chloride.—The general procedure for the sodium bicarbonate hydrolysis of sulfonyl chlorides was followed. A 65% yield of starting material was recovered. The product had the same ir as that of starting sulfonyl chloride, mp 52–57° (lit.¹ mp 62–64°).

Hydrolysis of α -Cyano- α,α -dichloromethylsulfonyl Chloride.—The general procedure for the sodium bicarbonate hydrolysis of sulfonyl chlorides was employed except that water was used in place of the bicarbonate solution. The product was distilled at 118–120° and had an ir spectrum identical with that of chloroacetonitrile, yield 37%.

General Procedure for Hydrolysis of Carbamoyl Chlorosulfines.—To 1 equiv of the sulfine in methanol was added *ca.* 10 equiv of sodium hydroxide solution. The volumes of methanol and water were approximately equal. After the solution was stirred 0.5 hr, concentrated hydrochloric acid was added until the solution became acidic. After standing *ca.* 1 hr the α -chloroacetamide was filtered and recrystallized from petroleum ether. When 9a was employed, *N*-isopropyl- α -chloroacetanilide was obtained in 66% yield: mp 67–68°; nmr (CDCl_3) τ 2.5 (m, 5), 5.1 (h, 1), 6.3 (s, 2), 8.9 (d, 6). Its ir spectrum was identical with that of authentic material (Monsanto). When 2b or 10 was employed as the sulfine, yields of 59 and 41%, respectively, of *m*-trifluoromethyl- α -chloroacetanilide were obtained: mp 69–70°; nmr (CDCl_3) τ 2.4 (m, 4), 5.9 (s, 2). The melting point of authentic material prepared from *m*-trifluoromethyl-aniline and chloroacetyl chloride was 74–75°.

General Procedure for the Potassium Hydroxide Hydrolysis of α,α -Dichlorosulfonyl Chlorides.—To 10 mmol of 9a in 50 ml of methanol was added 100 ml of 10% potassium hydroxide. After heating to 75°, the solution was acidified with concentrated hydrochloric acid. Cooling the mixture gave a 78% yield of *N*-isopropyl- α -chloroacetanilide (16a), mp 70–71° (petroleum ether).

Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{ClNO}$: C, 62.21; H, 6.60. Found: C, 62.01; H, 6.81.

In a similar manner 16b was prepared from 15b in 52% yield; 16c was prepared from 15c in 60% yield; 16d was prepared from 15d in 73% yield. In these cases, product identification was made on the basis of the nmr spectra.

Registry No.—2a, 36287-02-2; 2b, 36287-03-3; 2c, 36287-04-4; 2d, 36287-05-5; 2e, 36287-06-6; 2f, 36287-07-7; 2g, 36287-08-8; 3, 36287-09-9; 9a, 36287-10-2; 9b, 36287-11-3; 10, 36287-12-4; 14, 36208-06-7; 16a, 1918-16-7; *m*-trifluoromethyl- α -chloroacetanilide, 351-38-2.

S-Aroyl-, S-Thioaroyl-, and S-Imidoylhydrosulfamines

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Amination of sodium salts of aromatic thio acids with sodium hydroxylamine-*O*-sulfonate forms stable *S*-aroyl-hydrosulfamines, ArCOSNH_2 . The thio analogs, ArCSSNH_2 , and *N*-phenylimino analogs, $\text{RC}(=\text{NC}_6\text{H}_5)\text{SNH}_2$, are less stable. Reaction with isocyanates gives stable ureas. Cyclic imides and Schiff bases with salicylaldehyde have also been made.

S-Aroylhydrosulfamines, a new type of derivative, may be made simply by mixing aqueous solutions of sodium hydroxylamine-*O*-sulfonate and the sodium salt of an aromatic thio acid and filtering off the product.

Surprisingly, these compounds are, in general, stable to recrystallization, storage, and reaction with other reagents.

Previous attempts to make *S*-acylhydrosulfamines