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 sulfenyl 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-dichlorosulfenyl 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 (±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 ($M^+ - SO$). 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 ($M^+ - SO$, 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-thioxoacetamide[2] 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-dichloromethylsulfenyl Chloride.—The general procedure of sodium bicarbonate hydrolysis of α,α-dichlorosulfenyl 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-Phenylsulfenyl-α,α-dichloromethylsulfenyl Chloride.—The general procedure for the sodium bicarbonate hydrolysis of sulfenyl chlorides was followed. A 65% yield of starting material was recovered. The product had the same ir as that of starting sulfenyl chloride, mp 52–57° (lit.[1] mp 62–64°).

Hydrolysis of α-Cyano-α,α-dichloromethylsulfenyl Chloride.—The general procedure for the sodium bicarbonate hydrolysis of sulfenyl 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*-trifluoromethylaniline and chloroacetyl chloride was 74–75°.

General Procedure for the Potassium Hydroxide Hydrolysis of α,α-Dichlorosulfenyl 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 $C_{11}H_{14}ClNO$: 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*-aroylhydrosulfamines, $ArCOSNH_2$. The thio analogs, $ArCSSNH_2$, and *N*-phenylimino analogs, $RC(=NC_6H_5)SNH_2$, 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

TABLE I

S-AROYL-, S-THIOAROYL-, AND S-IMIDOYLHYDROSULFAMINES[a,b]

No.	Compd	Registry no.	Yield, %	Recrystn solvent	Mp, °C	Pmr ($CDCl_3$), NH_2, ppm
1	$C_6H_5COSNH_2$	25740-80-1	90	Et_2O	88.5–90	2.47
2	3,4-$Cl_2C_6H_3COSNH_2$	35124-68-6	95	CH_2Cl_2	119–120	2.83
3	p-$O_2NC_6H_4COSNH_2$	35124-67-5	41	$CHCl_3$	113–114	1.90
4	p-$CH_3OC_6H_4COSNH_2$	35124-66-4	94	Et_2O	99–100	2.78
5	p-$H_2NSCOC_6H_4COSNH_2$	35124-69-7	81	CH_3CN[c]	185 dec[c]	
6	1-Naphthoyl-SNH_2	35124-65-3	93	CCl_4	76.5–77	3.05
7	2-Furoyl-SNH_2	35124-70-0	70	CCl_4	60–61	2.90
8	$C_6H_5CSSNH_2$	35124-71-1	84	Pentane	29	3.21
9	p-$ClC_6H_4CSSNH_2$	35124-72-2	87	Hexane	60–61	3.31
10	$CH_3C(=NC_6H_5)SNH_2$	35124-73-3	88	CH_3OH	69.5–71	2.98
11	$C_6H_5C(=NC_6H_5)SNH_2$	35124-74-4	94	Cyclohexane	68–69	2.99

[a] M. S. Raasch, U. S. Patent 3,631,071 (1971). [b] Satisfactory analytical data (±0.40% for C, H, and N) were reported for all compounds listed in the table: Ed. [c] Low solubility; melting point determined by placing on hot block.

$$ArCOSNa + H_2NOSO_3Na \longrightarrow ArC(=O)SNH_2 + Na_2SO_4$$

have been recorded. Reaction of CH_3COSCl with diethylamine gave a product, presumably $CH_3COSN(C_2H_5)_2$, which soon decomposed to sulfur and diethylacetamide. Piperidine gave similar results. From aniline, the oil obtained, $CH_3COSNHC_6H_5$, underwent 50% decomposition in 24 hr at 3–5° and complete decomposition in 3 days.[1] Further, oxidative coupling of cyclohexylamine with ArCOSNa or ArCSSNa produced the amide or thioamide and sulfur. The reaction was postulated to proceed through the unstable *N*-cyclohexyl-*S*-aroylhydrosulfamine.[2]

The reported instability of *S*-acylhydrosulfamines and *N*-alkyl-*S*-aroylhydrosulfamines is in agreement with the present work. Reaction of sodium hydroxylamine-*O*-sulfonate with sodium thioacetate gave an immediate precipitation of sulfur. Similarly, sodium *N*-methylhydroxylamine-*O*-sulfonate[3] and sodium thiobenzoate resulted in a 90% yield of sulfur and *N*-methylbenzamide. Sodium 3,4-dichlorothiobenzoate reacted in the same manner. Sodium thionicotinate[4] and sodium hydroxylamine-*O*-sulfonate gave sulfur and nicotanamide. Thus, *S*-nicotinoylhydrosulfamine is also unstable.

Examples of *S*-aroylhydrosulfamines are listed in Table I (**1–7**). The *p*-nitro derivative is the least stable. Its preparation in 41% yield is accompanied by a 37% yield of *p*-nitrobenzamide from decomposition. The rest are stable except that the furoyl compound decomposes on long storage at 24°. The relative stability of the compounds was estimated by placing a melting point capillary tube containing the compound in a bath at 190° and noting the number of seconds required for the melt to become cloudy because of the liberation of sulfur. Exact times are subject to reservations as they appear to be influenced by catalytic amounts of impurities, but the times observed were p-$O_2NC_6H_4$, 6 sec; 2-furyl, 52; C_6H_5, 120; p-$CH_3OC_6H_4$, 250; 1-naphthyl, 373. For 3,4-$Cl_2C_6H_3$, all the sulfur stayed in solution.

S-Thioaroylhydrosulfamines.—The two thioaroyl analogs, $C_6H_5CSSNH_2$ and p-$ClC_6H_4CSSNH_2$, in Table I are less stable than any of the carbonyl compounds. Of the two, the *p*-chloro compound is the more stable. Both can be stored at −78°. Compounds of the type $ROCSSNH_2$, from sodium xanthates and sodium hydroxylamine-*O*-sulfonate, have been reported.[5] They are unstable. However, $(CH_3)_2NCSSNH_2$ from sodium dimethyldithiocarbamate and chloramine[6,7] or ammonia plus sodium hypochlorite[7] will last for months at 24°. This compound can also be made conveniently by using sodium hydroxylamine-*O*-sulfonate as the aminating agent.

S-Imidoylhydrosulfamines.—An imino analog, $C_6H_5C(=NC_6H_5)SNH_2$, of the *S*-aroyl- and *S*-thioaroylhydrosulfamines was synthesized by dissolving thiobenzanilide in aqueous sodium hydroxide and adding sodium hydroxylamine-*O*-sulfonate. The compound can be kept at 4°. From thioacetanilide $CH_3C(=NC_6H_5)SNH_2$ can be made but is less stable. The oxidative amination of substituted thioureas and thiourethanes with amines to form compounds of the type $R_2NC(=NR^1)SNR^2R^3$ and $ROC(=NR^1)SNR^2R^3$ has been reported.[8]

Derivatives.—The *S*-aroyl-, *S*-thioaroyl-, and *S*-imidoylhydrosulfamines react with isocyanates to form ureas (eq 1). These derivatives are stable, even those

$$RC(=X)SNH_2 \xrightarrow{R^1NCO} RC(=X)SNHCONHR^1 \quad (1)$$
$$X = O, S, NC_6H_5$$

prepared from unstable starting materials. Examples are listed in Table II.

Schiff bases have been formed from salicylaldehyde (eq 2 and 3). With p-$ClC_6H_4CSSNH_2$, however, a 76% yield of sulfur was obtained.

With *S*-aroylhydrosulfamines, amic acids and cyclic imides have been obtained from cyclic anhydrides, *e.g.*,

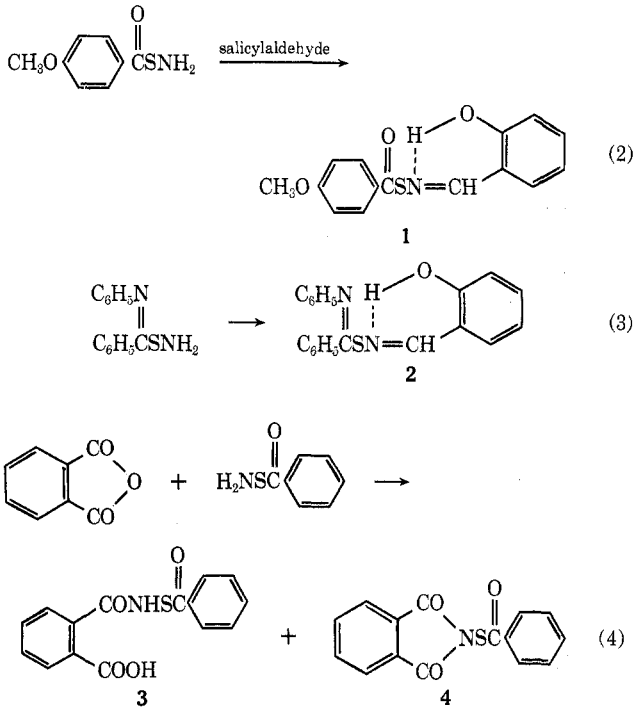
(1) H. Böhme and M. Clement, *Justus Liebigs Ann. Chem.*, **576**, 61 (1952).
(2) G. Alliger, G. E. P. Smith, Jr., E. L. Carr, and H. P. Stevens, *J. Org. Chem.* **14**, 962 (1949).
(3) E. Schmitz, R. Ohme, and D. Murawski, *Chem. Ber.*, **98**, 2516 (1965).
(4) A. M. Grigorovskii and Z. M. Kimen, *Z. Obshch. Khim.* **18**, 171 (1948); *Chem. Abstr.*, **42**, 7296 (1948).
(5) R. Gösl, *Angew. Chem.*, **74**, 329 (1962); *Angew. Chem., Int. Ed. Engl.*, **1**, 268 (1962); R. Gösl and A. Meuwsen, *Z. Anorg. Allg. Chem.*, **314**, 334 (1962), aminated sodium thiosulfate with sodium hydroxylamine-*O*-sulfonate to form H_2NSSO_3Na.
(6) R. S. Hanslick, U. S. Patent 2,318,482 (1943); *Chem. Abstr.*, **37**, 6159 (1943).
(7) G. E. P. Smith, Jr., G. Alliger, E. L. Carr, and K. C. Young, *J. Org. Chem.*, **14**, 935 (1949).
(8) K. Ley and U. Eholzer, *Angew. Chem.*, **78**, 672 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 674 (1966); German Patent 1,255,654 (1967); *Chem. Abstr.*, **68**, 87302*a* (1968); U. Eholzer, K. Ley, G. Zumach, L. Eue, and E. Hack, British Patent 1,074,760 (1968); *Chem. Abstr.*, **65**, 13605*b* (1966); H. Huckstadt, U. Eholzer, F. Moll, W. Himmelmann, and K. Ley, British Patent 1,129,356 (1968); *Chem. Abstr.*, **66**, 110062*s* (1967); D. Duerr, German Patent 1,936,459 (1970); *Chem. Abstr.*, **72**, 90119*j* (1970).

TABLE II

UREAS FROM REACTION WITH ISOCYANATES[a]

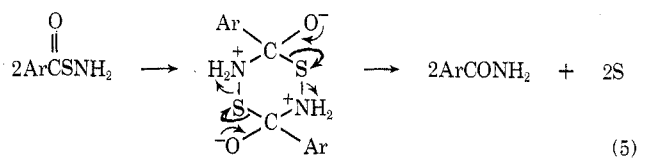
Compd	Registry no.	Recrystn solvent	Yield, %	Mp, °C
$C_6H_5COSNHCONHC_6H_5$	36504-30-0	Acetone	90	192.5–194
$C_6H_5COSNHCONH$-*p*-C_6H_4Cl	36504-31-1	Acetone	96	199–199.5
$C_6H_5COSNHCONHCH_3$	36504-32-2	Dioxane	69	194–195.5
3,4-$Cl_2C_6H_3COSNHCONHCH_3$	36504-33-3	Dioxane	98	195–196
$C_6H_5CSSNHCONHC_6H_5$	36504-34-4	Dioxane	88	179–180
$CH_3C(=NC_6H_5)SNHCONH$-*p*-C_6H_4Cl	36504-35-5	CH_2Cl_2	70	134–136
$C_6H_5C(=NC_6H_5)SNHCONHCH_3$	36504-36-6	EtOAc	78	141.5–142

[a] Satisfactory analytical data (±0.38% for C, H, and N) were reported for all compounds listed in the table: Ed.



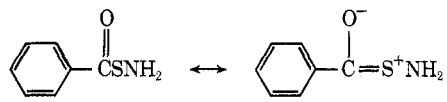
eq 4. 4-Cyclohexene-1,2-dicarboxylic and dichloromaleic anhydrides are also operable.

Discussion of Stability.—The decomposition of the *S*-aroylhydrosulfamines to amide and sulfur could occur by a unimolecular homolytic or heterolytic mechanism, but we favor a bimolecular process involving a cyclic intermediate or transition state which could decompose in a concerted manner to expel sulfur and form the amide (eq 5). Such a mechanism would be expected to



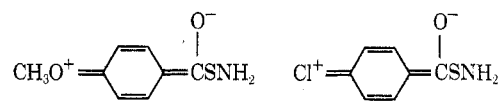
show substituent effects analogous to basic hydrolysis of esters as one factor affecting stability. The *p*-nitro group, for example, markedly reduces stability. The more basic *N*-methyl derivatives might form the transition state more readily, causing the observed instability, whereas *N*-acyl derivatives are more stable than the parent compounds. In the case of compounds of the type $ArC(=S)SNH_2$, the preference of sulfur to be singly bonded would favor the transition state and result in the observed lower stability compared to the carbonyl compounds.

The fact that *S*-aroylhydrosulfamines are stable in contrast to their aliphatic analogs can be rationalized by the additional resonance conjugation

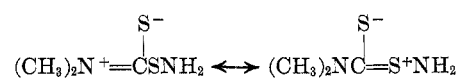


Electron donation by *N*-methyl lessens the contribution of the sulfonium form and results in instability while N-acylation has the reverse effect.

In the case of *p*-methoxy and *p*-chloro derivatives, an additional resonance form is favorable.



These representations can be regarded as vinylogous to the thioamide type of stabilization which probably occurs with $(CH_3)_2NCSSNH_2$ to make it more stable than $ArCSSNH_2$.



Experimental Section

The ^1H nmr spectra were determined on a Varian A-60 instrument using tetramethylsilane as internal standard. The ir spectra were measured on Perkin-Elmer Model 21. Melting points are uncorrected.

Monothio Acids.—Except for thiobenzoic acid and dithioterephthalic acid, which can be purchased, the thio acids were made by the procedure of Noble and Tarbell.[9] In preparing thionicotinic acid,[4] the reaction was run at −20°. The acid was precipitated with acetic acid and recrystallized from 50% ethanol, yield 43%. *p*-Thioanisic,[10] *p*-nitrothiobenzoic,[11] 1-thionaphthoic,[12] and 2-thiofuroic[13] acids have been reported previously. 3,4-Dichlorothiobenzoic acid is new, mp 73.5–75° from CCl_4.

Anal. Calcd for $C_7H_4Cl_2OS$: C, 40.58; H, 1.95; S, 15.48. Found: C, 40.84; H, 1.96; S, 15.04.

***S*-Aroylhydrosulfamines (Table I).**—The general procedure was to prepare a *ca.* 30% solution of sodium hydroxylamine-*O*-sulfonate by neutralizing an aqueous solution of the acid with aqueous sodium hydroxide below 20°. This was added slowly to a *ca.* 15%, mechanically stirred solution of the sodium salt of the thio acid below 20° until no more precipitation occurred. The product was filtered and air-dried. The yields before recrystallization appear in the table. In the case of the preparation of *S*-(*p*-nitrobenzoyl)hydrosulfamine, the dried product mixture was stirred with chloroform, and *p*-nitrobenzamide was filtered. The product was crystallized from the filtrate with a minimum of heating for concentration: ir for $C_6H_5COSNH_2$ 3333, 3268

(9) P. Noble, Jr., and D. S. Tarbell in "Organic Syntheses," Collect. Vol IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, pp 924–927.

(10) I. Bloch and M. Bergmann, *Ber. Deut. Chem. Ges. B*, **53**, 961 (1920).

(11) A. M. Khaletskii and A. M. Yanovitskaya, *Z. Obshch. Khim.*, **19**, 1193 (1949); *J. Gen. Chem. USSR*, **19**, 1187 (1949).

(12) S. I. Sergievskaya and A. A. Kropacheva, *Z. Obshch. Khim.*, **10**, 1737 (1940); *Chem. Abstr.*, **35**, 4003 (1941).

(13) S. Patton, *J. Amer. Chem. Soc.*, **71**, 3571 (1949).

cm^{-1} (NH_2), 1658 (C=O), 1595, 1580, 1488 (aromatic C=C), 689 (monosubstituted aromatic).

S-Thiobenzoylhydrosulfamine (Table I).—An alcoholic solution of potassium dithiobenzoate was prepared from benzotrichloride and potassium sulfide according to the directions of Kurzer and Lawson.[14] The alcohol was removed under reduced pressure, and the residual salt was dissolved in 200 ml of water and extracted with ether. The aqueous layer was separated and acidified with 25 ml of 37% hydrochloric acid. The dithiobenzoic acid was collected with two 150-ml portions of ether and dried (Na_2SO_4), and the ether was removed to leave 25 g of a purple oil. This crude dithiobenzoic acid was aminated according to the general procedure described above. The orange, crystalline *S*-thiobenzoylhydrosulfamine was filtered while the aqueous phase was at 15°, yield 23 g. It can be stored at −78°.

***S*-(*p*-Chlorothiobenzoyl)hydrosulfamine (Table I).**—Crystalline *p*-chlorodithiobenzoic acid[15] was prepared according to the procedure used for dithiobenzoic acid except that *p*-chlorobenzotrichloride was used, yield 66%. It was aminated in the usual way: ir of *p*-$ClC_6H_4CSSNH_2$ 3300, 3205 cm^{-1} (NH_2), 3077 (=CH), 1590, 1481 (aromatic C=C), 830 (para-disubstituted aromatic). The compound can be stored at −78°.

***S*-(*N*-Phenylacetimidoyl)hydrosulfamine (Table I).**—Thioacetanilide (25 g, 0.166 mol) was dissolved in 200 ml of water containing 7 g (0.175 mol) of sodium hydroxide. Addition below 20° of 22.6 g (0.2 mol) of hydroxylamine-*O*-sulfonic acid in 45 ml of water neutralized below 20° with 8 g (0.2 mol) of sodium hydroxide in 45 ml of water caused precipitation of the product. This unstable compound was filtered and blotted on paper, yield 24 g. An analytical sample was quickly recrystallized from methanol. The compound can be stored at −78°: ^1H nmr ($CDCl_3$) 1.93 ppm (s, CH_3), 2.98 (s, broad, NH_2, removed by D_2O), 6.7–7.5 (m, C_6H_5).

***S*-(*N*-Phenylbenzimidoyl)hydrosulfamine (Table I).**—Thiobenzanilide (42.7 g, 0.2 mol) was dissolved in 400 ml of water containing 16 g (0.4 mol) of sodium hydroxide. Amination was accomplished by adding below 20° with stirring a solution of 27 g (0.24 mol) of hydroxylamine-*O*-sulfonic acid in 60 ml of water neutralized with 9.6 g (0.24 mol) of sodium hydroxide in 60 ml of water. The initial addition produced a sticky precipitate which was scratched to provide seed crystals. The product was filtered and air-dried to give 43 g (94%). Recrystallization twice from cyclohexane left 28 g (61%), mp 68–69°. An additional 5 g (11%) was isolated from the mother liquor: ir 3311, 3145 cm^{-1} (NH_2), 3058, 3012 (=CH), 1616 (C=N), 1585, 1572, 1479 (aromatic C=C), 770–667 (monosubstituted aromatic); Raman 1621 cm^{-1} (C=N), 1592 (aromatic C=C). This compound decomposes in days or weeks at 24°, the rate being dependent on purity. The decomposition products are sulfur and benzamidine, mp 115–116°.

Ureas (Table II).—The reaction of the hydrosulfamines with isocyanates was carried out in dichloromethane. After 20 hr the precipitated urea was filtered. The mother liquid was concentrated in some cases to obtain more product. Yields before recrystallization are recorded in the table: ^1H nmr for C_6H_5-$COSNHCONHC_6H_5$[$(CD_3)_2SO$] 6.6–7.9 ppm (m, 2 C_6H_5), 7.84 (s, NHS), 8.94 (s, NHCO). The NH peaks were removed by D_2O.

***S*-(*p*-Anisoyl)-*N*-salicylidenehydrosulfamine (1).**—*S*-(*p*-Anisoyl)hydrosulfamine (3.66 g, 0.02 mol) and 2.44 g (0.02 mol) of salicylaldehyde were heated on a steam bath for 30 min. The mixture first melted and then solidified. Recrystallization from dioxane gave 4.9 g (85%) of the Schiff base, mp 186–187.5°.

Anal. Calcd for $C_{15}H_{13}NO_3S$: C, 62.68; H, 4.56; S, 11.16. Found: C, 62.45; H, 4.60; S, 11.06.

(14) F. Kurzer and A. Lawson, *Org. Syn.*, **42**, 100 (1942).

(15) F. Becke and H. Hagen, German Patent 1,274,121 (1968); *Chem. Abstr.*, **70**, 3573v (1969); R. Mayer and S. Scheithauer, *Chem. Ber.*, **98**, 829 (1965); K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, **15**, 1087 (1961).

***S*-(*N*-Phenylbenzimidoyl)-*N*-salicylidenehydrosulfamine (2).**—*S*-(*N*-Phenylbenzimidoyl)hydrosulfamine (4.56 g, 0.02 mol) and 2.44 g (0.02 mol) of salicylaldehyde were heated on a steam bath for 30 min. The resulting solid was recrystallized from carbon tetrachloride to give 4.22 g (64%) of the Schiff base, mp 139–139.5°.

Anal. Calcd for $C_{20}H_{16}N_2OS$: C, 72.25; H, 4.85; N, 8.43. Found: C, 71.96; H, 4.73; N, 8.37.

***N*-(Benzoylthio)phthalimide (4) and *N*-(Benzoylthio)phthalamic Acid (3).**—To 8.9 g (0.06 mol) of phthalic anhydride dissolved in in 30 ml of warm tetrahydrofuran was added 9.2 g (0.06 mol) of *S*-benzoylhydrosulfamine in 20 ml of tetrahydrofuran. The solution was refluxed for 30 min, and the solvent was then allowed to evaporate. The resulting crystals were rinsed with carbon tetrachloride, dried, and stirred with 5% sodium bicarbonate solution. The phthalimide was filtered, yield 8.3 g (49%). Recrystallization from acetone left 7.1 g, mp 150–151°.

Anal. Calcd for $C_{15}H_9NO_3S$: C, 63.63; H, 3.20; S, 11.32. Found: C, 63.82; H, 3.27; S, 11.16.

The sodium bicarbonate filtrate was acidified with hydrochloric acid and the *N*-(benzoylthio)phthalamic acid was filtered, washed with water, and air-dried, yield 5.3 g (29.5%). Recrystallization from acetone gave 4.1 g in two crops, mp 144–144.5°, with conversion into the phthalimide.

Anal. Calcd for $C_{15}H_{11}NO_4S$: C, 59.78; H, 3.68; S, 10.64. Found: C, 59.86; H, 3.76; S, 10.81.

6-[(1-Naphthoylthio)carbamoyl]-3-cyclohexene-1-carboxylic Acid.—*S*-(1-Naphthoyl)hydrosulfamine (6.09 g, 0.03 mol) in 25 ml of chloroform was added to 4.56 g (0.03 mol) of 4-cyclohexene-1,2-dicarboxylic anhydride in 25 ml of chloroform, and the solution was refluxed for 1 hr. From the cooled solution, 7.96 g (75%) of the amic acid was filtered. It was completely soluble in 5% sodium bicarbonate. Recrystallization from acetone left 6.1 g mp 172.5–173°.

Anal. Calcd for $C_{19}H_{17}NO_4S$: C, 64.21; H, 4.82; N, 3.94. Found: C, 64.20; H, 4.86; N, 3.86.

***N*-(1-Naphthoylthio)-4-cyclohexene-1,2-dicarboximide.**—The above amic acid (5.33 g, 0.15 mol), 10 ml of pyridine, and 1.6 ml (0.017 mol) of acetic anhydride were mixed and allowed to stand 1 hr. The solution was poured into water, and the crystals were filtered and air-dried. The product was taken up in acetone, and 0.8 g of insoluble material was filtered. The acetone was evaporated, and the residue was recrystallized twice from ethanol to give 3.5 g (70%) of the imide, mp 96–98°.

Anal. Calcd for $C_{19}H_{15}NO_3S$: C, 67.64; H, 4.48; N, 4.15. Found: C, 67.31; H, 4.46; N, 4.00.

***N*-(3,4-Dichlorobenzoylthio)dichloromaleimide.**—Dichloromaleic anhydride (2.50 g, 0.015 mol), 3.33 g (0.015 mol) of *S*-(3,4-dichlorobenzoyl)hydrosulfamine, and 10 ml of benzene were heated under reflux on a steam bath for 30 min, then 2 hr with the condenser removed. The residue was recrystallized twice from cyclohexane to give 4.02 g (71%) of the imide, mp 89–91°.

Anal. Calcd for $C_{11}H_3Cl_4NO_3S$: C, 35.61; H, 0.82; N, 3.78. Found: C, 35.62; H, 0.82; N, 3.72.

Registry No.—**1**, 36504-37-7; **2**, 36504-38-8; **3**, 36504-39-9; **4**, 36504-40-2; 6-[(1-naphthoylthio)-carbamoyl]-3-cyclohexene-1-carboxylic acid, 36504-41-3; *N*-(1-naphothylthio)-4-cyclohexene-1,2-dicarboximide, 36504-42-4; *N*-(3,4-dichlorobenzoylthio)dichloromaleimide, 36504-43-5; 3,4-dichlorothiobenzoic acid, 36504-44-6.

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