ics", J. P. Snyder, Ed., Academic Press, New York, N.Y., 1969; Chapter 4; W. Baker and W. D. Ollis, *Q. Rev., Chem. Soc.*, **11**, 15 (1957).
(6) A. Schönberg and E. Frese, *Chem. Ber.*, **103**, 3885 (1970).
(7) K. Inouye, S. Sato, and M. Ohta, *Bull. Chem. Soc. Jpn.*, **43**, 1911 (1970).
(8) K. T. Potts and D. McKeough, unpublished results.
(9) (a) M. Ohta and M. Sugiyama, *Bull. Chem. Soc. Jpn.*, **38**, 596 (1965); (b) M. Ohta and M. Sugiyama, *Ibid.*, **36**, 1437 (1963); (c) E. Campaigne, R. D. Hamilton, and N. W. Jacobsen, *J. Org. Chem.*, **27**, 1708 (1964).
(10) C. V. Greco, R. P. Gray, and V. G. Grosso, *J. Org. Chem.*, **32**, 4101 (1967).
(11) K. T. Potts and S. Husain, *J. Org. Chem.*, **36**, 3368 (1971).
(12) (a) A. Lawson and C. E. Searles, *J. Chem. Soc.*, 1556 (1957); (b) M. Ohta and C. C. Shin, *Bull. Chem. Soc. Jpn.*, **38**, 704 (1965); (c) K. T. Potts, J. Baum, E. Houghton, D. N. Roy, and U. P. Singh, *J. Org. Chem.*, **39**, 3619 (1974).
(13) H. Gotthardt and B. Christl, *Tetrahedron Lett.*, 4743 (1968).
(14) K. T. Potts, E. Houghton, and U. P. Singh, *J. Org. Chem.*, **39**, 3627 (1974).
(15) Attempts to use the in situ technique with the precursor to **2** and the dipolarophile were unsuccessful in most instances.
(16) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2d ed, Pergamon Press, Oxford, 1969, p 209.
(17) H. Gotthardt and B. Christl, *Tetrahedron Lett.*, 4747 (1968).
(18) H. Gotthardt and B. Christl, *Tetrahedron Lett.*, 4751 (1968).
(19) M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, **88**, 4112 (1962); **89**, 3639 (1967); F. H. M. Deckers, W. N. Speckamp, and H. O. Huisman, *Chem. Commun.*, 1521 (1970); M. P. Cava and G. E. M. Husbands, *J. Am. Chem. Soc.*, **91**, 3952 (1969).
(20) K. T. Potts, J. Baum, and E. Houghton, *J. Org. Chem.*, **39**, 3631 (1974).
(21) H. Matsukubo and H. Kato, *J. Chem. Soc., Chem. Commun.*, 412 (1974).
(22) D. J. Anderson and A. Hassner, *Synthesis*, 483 (1975).
(23) V. Nair, *J. Org. Chem.*, **37**, 2508 (1972); A. Hassner and D. J. Anderson, *Ibid.*, **39**, 2031 (1974).
(24) Spectral characterizations were carried out with the following instrumentation: ir, Perkin-Elmer Model 337 infrared spectrophotometer; uv, Cary Model 14 spectrophotometer; NMR, Varian A-60 and T-60 spectrometers using Me_4Si as internal standard; mass spectra, Hitachi-Perkin Elmer RMU-6E mass spectrometer at 70 eV using the direct insertion probe at a temperature of ca. 150 °C. Evaporations were done under reduced pressure using a rotatory evaporator and melting points were determined in capillaries. Microanalyses are by Galbraith Laboratories, Inc., Knoxville, Tenn., and Instranal Laboratories, Rensselaer, N.Y.
(25) K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, **15**, 1087 (1961).
(26) The α and β nomenclature used refers to the orientation of the substituent with respect to the sulfur bridge.

Preparation and Physical and Chemical Properties of "Free" Sulfilimines[1]

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Received July 30, 1975

N-p-Tosylsulfilimines, when dissolved in concentrated sulfuric acid, are converted to the corresponding *p*-toluenesulfonic acid salts of sulfilimines which upon treatment with alkali give "free" sulfilimines in good yields. Diaryl sulfilimines are relatively stable crystalline compounds, while dialkyl or alkyl aryl derivatives are unstable and decompose readily at room temperature to form the corresponding sulfides and ammonia. The structure of "free" sulfilimine was identified by spectroscopic and elemental analyses. Some of the interesting chemical behavior of "free" diphenylsulfilimines is described.

The acid-catalyzed hydrolysis of *N-p*-tosylsulfilimine is known to give the corresponding sulfoxide in high yield.[2] The mechanism for the hydrolysis has been explored kinetically by Kucsmann and his co-workers[3] using *N*-arylsulfonyl alkyl aryl sulfilimines in moderately concentrated aqueous sulfuric acid or perchloric acid. On the basis of the kinetic investigations, the reaction mechanism for the hydrolysis was explained in terms of the nucleophilic attack of water on the positively polarized S(III) atom of the protonated sulfilimine. Meanwhile, we found recently that the treatment of *N-p*-tosylsulfilimines with concentrated sulfuric acid gave the corresponding "free" sulfilimine nearly quantitatively.[4]

Earlier methods of preparation of free sulfilimines have been reported by Appel[5] from dialkyl or *p,p'*-dimethoxydiphenyl sulfide with chloramine or hydroxylamine sulfate. Similarly, Lambert and his co-workers[6] prepared pentamethylenesulfilimine and presented spectroscopic data. Recently Tamura et al.[7] also found a new method which involves treatment of the sulfides and *O*-mesitylenesulfonyl hydroxylamine. More recently, a method which uses diaryl alkoxy sulfurane and ammonia has been described by Martin.[8] However, each of these reactions has some shortcomings for a general synthetic procedure to prepare free sulfilimines. We have now found that any kind of *N-p*-tosylsulfilimine can be synthesized readily under certain set conditions from the corresponding sulfides and chloramine-T and their free sulfilimines are readily obtained as salts simply by dissolving them in concentrated sulfuric acid. This synthetic method is the first general procedure for the preparation of varied sulfilimines in large quantities; we now present the details of this procedure and a few pertinent physical and chemical characteristics of the sulfilimines.

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Results and Discussion

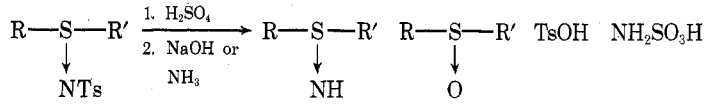
Diaryl Sulfilimines. Cleavage of diphenyl-*N*-tosylsulfilimine (I) was carried out in 95% sulfuric acid at room temperature. After quenching in ice, the tosylate salt III could be extracted with chloroform. The free sulfilimine (II) crystallized on basifying a solution of III. The imine II has a strong ir absorption band at 940 cm^{-1} which is assigned as –S–N– bond, while other strong absorption bands appear at 2350 (OH) and 3120 cm^{-1} (NH), respectively. The NMR signals of II are δ 7.20–7.70 (10 H, phenyl), 2.1 ppm (1.7 H, NH and OH). The mass spectrum of II was identical with that of diphenyl sulfide; the parent peak due to the free sulfilimine did not appear at all, indicating that the S–N bond of II is weak and is cleaved readily.

The structure of II was confirmed by treatment with tosyl chloride under alkaline condition to give the starting *N-p*-tosylsulfilimine (I) quantitatively. Furthermore, II was hydrolyzed to diphenyl sulfoxide upon heating at 65 °C for 3 h in 20% aqueous sulfuric acid solution. However, II was stable at even relatively strong alkaline conditions and did not react at all in aqueous 20% sodium hydroxide solution at an elevated temperature. The reactions are summarized in Scheme I.

Data for the cleavage of other diaryl *N-p*-tosylsulfilimines are summarized in Table I.

Preparation of Alkyl Aryl and Dialkyl Sulfilimines.

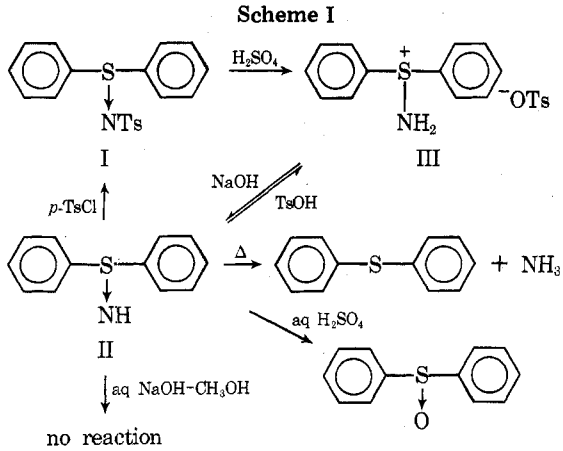
Table I. Products and Yields in the Reaction of *N*-*p*-Tosylsulfilimine with Concentrated Sulfuric Acid



Run	R	R′	Reaction condition r[a]	Temp	Time		Product yields, % II (mp, °C)	IV	V	VI
1	C_6H_5	C_6H_5	2	r.t.	10 min	B	90 (74)[b]			
2	C_6H_5	C_6H_5	5	r.t.	24 h	B		95		
3	C_6H_5	C_6H_5	1	r.t.	24 h	A	24	51		70
4	*p*-$CH_3C_6H_4$	C_6H_5	2	r.t.	10 min	B	95 (54.5–55.5)[c]			
5	*o*-$CH_3C_6H_4$	C_6H_5	2	r.t.	10 min	B	97 (83.5–84.5)[c]			
6	*p*-ClC_6H_4	C_6H_5	2	r.t.	10 min	B	77 (48–49)[c]			
7	*m*-ClC_6H_4	C_6H_5	2	r.t.	10 min	B	(35–36)[c]			
8	*p*-$NO_2C_6H_4$	C_6H_5	2	r.t.	10 min	B	95 (98–99)[c]			
9	*o*-$NO_2C_6H_4$	C_6H_5	2	r.t.	10 min	B	79 (104–104.5)[c]			
10	CH_3	C_6H_5	2	r.t.	5 min	B		97	55	
11	CH_3	C_6H_5	2	r.t.	5 min	A	95 (112–112.5)[d]			
12	CH_3	C_6H_5	1	r.t.	15 min	A		90		83
13	CH_3	*p*-$CH_3C_6H_4$	2	r.t.	5 min	A	95 (158–159)[d]			
14	C_2H_5	C_6H_5	2	40	15 min	A	95 (90–91)[d]		58	
15	C_2H_5	C_6H_5	2	40	15 min	B		96		
16	*c*-C_3H_5	*p*-$CH_3C_6H_4$	2	40	15 min	A	95 (138–139)[d]			
17	CH_3	CH_3	2	40	10 min	A	95 (103–104)[d,e]			
18	C_2H_5	C_2H_5	2	40	10 min	A	95 (110–111)[d]			
19	$-(CH_2)_5-$		2	40	15 min	A	95 (191)		72	
20	$-(CH_2)_5-$		1	r.t.	48 h	A		30[f]		96

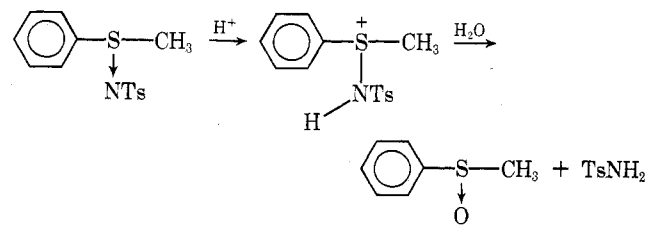
[a] Method A, the acid solution was quenched in cold ether; B, the acid solution was poured onto ice–water. r = ratio, H_2SO_4 (ml)/I (g). [b] Monohydrate. [c] Anhydrous. [d] As picrate. [e] Lit. mp. 111 °C.[5] [f] Corresponding sulfide (20%) was obtained as other product.

Scheme I



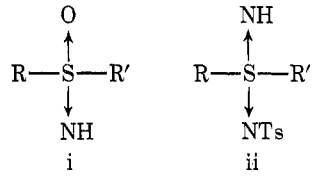
Although diaryl sulfilimines can be prepared readily as illustrated in the case of diphenyl-*N*-*p*-tosylsulfilimine, similar treatment of *N*-*p*-tosyl dialkyl or alkyl aryl sulfilimines with concentrated sulfuric acid did not give the corresponding free sulfilimines but rather the corresponding sulfoxides (runs 9, 14). However, in these reactions *p*-tosylamide, which is usually the by-product of the direct hydrolysis of the sulfilimine to the sulfoxide, was not isolated at all. This suggests that the formation of the sulfoxide does not occur by direct hydrolysis of the *N*-*p*-tosylsulfilimine but by hydrolysis of the initially formed free sulfilimine when the sulfuric acid solution is quenched with ice–water. To avoid hydrolysis of the free sulfilimine, the sulfuric acid solutions of dialkyl or alkyl aryl sulfilimines were added to cold ethyl ether; the oily material which separated was identified as the bisulfate salts of the respective sulfilimines. The free sulfilimines were obtained by treatment of their acetone–methanol solutions with liquid ammonia (runs 10, 12, 13, 15–18). Generally, dialkyl or alkyl aryl free sulfilimines are unstable and decompose readily to the corresponding sulfides and ammonia. Therefore, these sulfilimines should be converted to the picrates as soon as they are isolated. The yields are summarized in Table I.

Chemical Properties of Free Sulfilimines. Reaction Mechanism. The hydrolysis of aryl methyl *N*-*p*-tosylsulfilimines is known to give the corresponding sulfoxides under both acidic and alkaline conditions.[2a] The stereochemical results indicate that under alkaline conditions, the hydrolysis proceeds by an SN2 reaction at sulfur since the configuration of the sulfoxide obtained is completely inverted. Under acidic conditions, the reactions are not stereospecific and yield the racemized sulfoxides. In acid, therefore, prior S–N bond cleavage must occur before nucleophilic attack on sulfur by a water molecule. Recently, Kucsmann et al.[3] studied the hydrolysis of methyl aryl *N*-*p*-arylsulfonylsulfilimines in aqueous sulfuric acid. Based on the Hammett equation and Bunnett–Olsen's values, they suggested that the hydrolysis proceeded by preequilibrium protonation of the imino nitrogen, followed by rate-determining nucleophilic attack of a water molecule. ^{18}O-Labeled sulfoxides, treated under



aqueous acidic conditions, undergo ^{18}O exchange with the medium even in concentrated sulfuric acid.[9] All these data show clearly that either S(III)–N or S(III)–O bond cleavage takes place under acidic reaction conditions. However, our new experimental results indicate that the *N*-*p*-tosylsulfilimine undergoes exclusively N–S(IV) bond cleavage upon treatment with concentrated sulfuric acid. The reaction is very facile and complete within a few minutes. A similar N–S(IV) bond cleavage is observed when an *N*-*p*-tosylsulfoximine[10] or sulfone diimine[11] is treated with concentrated sulfuric acid. For

Table II. Ir Stretching Absorption of Sulfilimine[a]



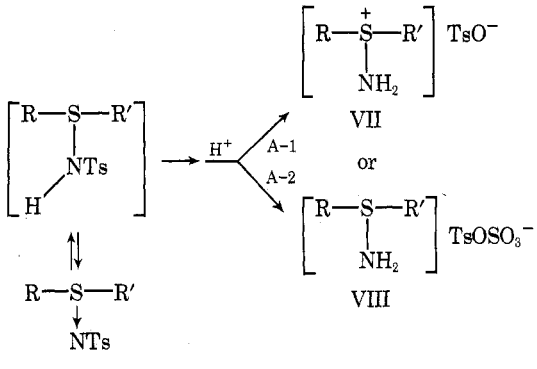
i ii

Compd	C_6H_5, C_6H_5	p-$CH_3C_6H_4$	$-(CH_2)_5-$
Free sulfilimine	940	920	900
N-p-Tosylsulfilimine	960	970	985
Sulfoximine[b]	965, 980 1095, 1130	980, 1090[26] 1220	
Sulfone diimine[c]	955, 1080[11]	970, 1050[26]	1010, 1040[11]

[a] In KBr. [b] i. [c] ii.

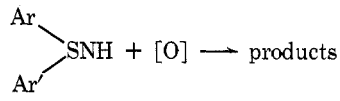
preparation of sulfilimines, the reaction should be carried out with 90–95% sulfuric acid within 10–15 min. The product obtained after longer reaction time (24 h) with 90–95% sulfuric acid was no longer free sulfilimine but the sulfoxide, together with toluenesulfonic acid which was identified as the thiuronium salt (run 2). When I was treated with 80% sulfuric acid at room temperature for 24 h, the N-p-tosylsulfilimine was recovered in 63% yield together with diphenyl sulfoxide (25%). Treatment of I with 50% sulfuric acid led to its complete recovery. Furthermore, when the N-p-tosylsulfilimine was dissolved in a small amount of 95% sulfuric acid or in 98% sulfuric acid and the solution was kept standing for prolonged reaction time (runs 3, 11, 19 in Table I) crystalline sulfamic acid (VI) precipitated.

Apparently, water molecules are in the form of oxonium ions and hence do not participate as a nucleophile in the initial S(IV)–N bond cleavage either by way of A-1 type or A-2 type mechanism. Instead, hydrogen sulfate ion should work as the nucleophile eventually affording the aminosulfonium salt VII or VIII as shown below.



Free sulfilimines thus obtained are generally oily materials except for diaryl derivatives. Therefore, the spectroscopic analysis is recommended for the identification. Free sulfilimines are relatively strong bases (pK_a = 8.5 for diaryl[13]). As shown in the Experimental Section, free sulfilimines have characteristic strong bands at 930–960 cm^{-1} due to S–N stretching band and 3120 cm^{-1} (NH). The position of the characteristic S–N ir band at around 940 cm^{-1} depends on the structure of the sulfilimine. In the case of diaryl compounds, electron-withdrawing substituents shift the band to the longer wavelength while the electron-donating groups do the opposite. In the case of alkyl aryl or dialkyl sulfilimines, the –S–N– absorption bands appear at the region of 900–910 cm^{-1}. The nature of the S–N band, namely whether the bond has semipolar single or double bond character, was discussed earlier with N-p-tosyl derivatives[14] and the former was favored. The several ir bands due to S–N bonds are shown. The characteristic S–N band of free sulfilimines is at lower wavenumber

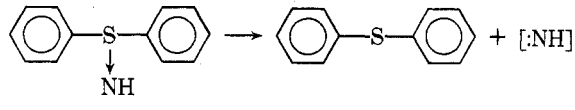
Table III. Oxidation Products of Free Sulfilimine



Ar	Ar′	Oxidant	Products (yields, %)
C_6H_5	C_6H_5	$KMnO_4$	Sulfoximine (95)
p-$CH_3C_6H_4$	C_6H_5	$KMnO_4$	Sulfoximine (95)
p-$NO_2C_6H_4$	C_6H_5	$KMnO_4$	Sulfoximine (80)
C_6H_5	C_6H_5	H_2O_2	Sulfoxiimine (30), sulfone (20), sulfoxide (20)
C_6H_5	C_6H_5	p-$CH_3C_6H_4CO_3H$	Sulfoxiimine (40), sulfone (20), sulfoxide (trace)
C_6H_5	C_6H_5	HNO_3	Sulfoxide (95)

than that of N-p-tosyl derivative or sulfoximine. Thus, the S–NH bond is even more semipolar than that of N-p-tosyl derivatives (Table II).

Pyrolysis of Free Sulfilimine. Even though the diaryl free sulfilimines are relatively stable, they decompose readily when heated in situ at 100 °C and afforded the sulfide and ammonia.[15] A detailed account of the pyrolysis of free sulfilimine



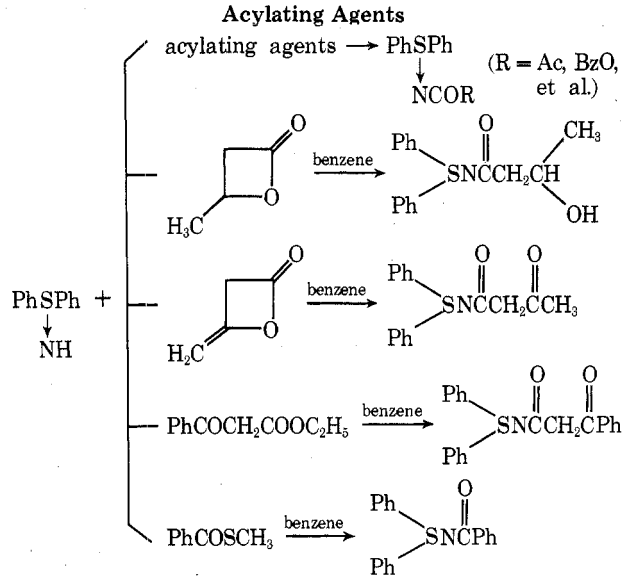
will be described elsewhere. This facile pyrolysis, as compared to that of the corresponding N-p-tosyl derivative, seems to support the conclusion that the S–N bond cleaves very readily forming the sulfide and nitrene which then disproportionates to ammonia.[15,16] The thermal instability of the free sulfilimine is consistent with both the GLC behavior and the mass spectroscopic pattern, which are the same as those of the corresponding sulfide.

Oxidation of Free Sulfilimines. Sulfoximines have hitherto been prepared from the corresponding sulfoxide by either treating with hydrazoic acid[17] or reacting with sulfonyl azide[18] or chloramine-T[19] in the presence of copper. Another alternative procedure is the permanganate oxidation of the N-acylsulfilimine.[20] However, none of these methods is general for the large-scale preparation of all kinds of sulfoximines. Thus it is difficult to prepare the diaryl sulfoximine, while it is dangerous to use a large quantity of toxic and explosive hydrazoic acid. However, because of the interesting pharmacological properties a general and convenient synthetic method of free sulfoximines has long been sought. Thus, the direct oxidation of free sulfilimines was carried out with various oxidizing agents, i.e., potassium permanganate, peracid, or hydrogen peroxide and diaryl sulfoximines having various substituents were successfully obtained in good yields. Generally, the oxidation of free sulfilimine was carried out in methanol solution of the sulfilimine. After the solution was refluxed for 1 h, it was worked up as usual, affording diphenylsulfoximine quantitatively. The sulfoximine was identified by both spectroscopic and elemental analyses. The oxidation was carried out similarly by other oxidizing reagents. The results are summarized in Table III.

As shown in Table III, the best results are obtained when the reaction is carried out with potassium permanganate, while the reaction with peracid or hydrogen peroxide gives a mixture of sulfoximine, sulfone, and sulfoxide. In the case of nitric acid, the sulfoxide was the sole product. This fact indicates that the acid-catalyzed hydrolysis took place during the reaction, affording the sulfoxide.

These sulfoximines have strong ir absorption bands at 940–960 (–S=N–), 1020–1040 (SO), 3300–3400 cm^{-1} (NH).

Scheme II. Reaction of Free Sulfilimine with Acylating Agents



In NMR, there are peaks at 3–4 (–NH–) and 7–8 ppm (phenyl H).

Reaction with Acylating Agents. Previously, we reported a convenient method for the preparation of various *N*-acylsulfilimines from diphenyl free sulfilimine and various acylating agents.[13] Recently, various acylated sulfilimines such as *N*-sulfonyl-,[21] *N*-acyl-,[22] *N*-ethoxycarbonyl-,[22] and *N*-carbamoylsulfilimines[23] were similarly prepared and some of their physical properties are summarized. The preparation of *N*-acyl derivatives from free sulfilimines is very simple. Acylation is completed in a few minutes just by dissolving equimolar amounts of free sulfilimine and acylating agent in benzene at room temperature. Acylating agents used are $(RCO)_2O$, RCOCl, TsCl, RNCO, and EtOC(O)Cl. Furthermore, four- and five-membered lactones, ketene dimer, esters[24] having electron-withdrawing groups such as ethyl acetoacetate or ethyl benzoylacetate, and thioesters also react with free sulfilimines and afforded the *N*-acyl substituted sulfilimines as shown in Scheme II. The *N*-acylsulfilimines having either a hydroxy or a carbonyl group in the molecules are not known and therefore this method is a convenient synthetic procedure for the preparation of such sulfilimine derivative.

The products, their yields, and some spectral data are summarized in the Experimental Section.

Experimental Section

***N*-*p*-Tosylsulfilimines.** All the sulfilimines were prepared by the Mann–Pope reaction by allowing the sulfides to react with chloramine-T.[25]

***S,S*-Diphenylsulfilimine (II). Method A.** Diphenyl-*N*-*p*-tosylsulfilimine (1 g, 0.28 mmol) was dissolved in 1 ml of concentrated sulfuric acid (95% commercial) at room temperature. The solution was kept for 10 min and then poured onto ice. The oily product precipitated out immediately. The aqueous solution was extracted with chloroform. After chloroform was removed, the residue solidified to afford quantitatively the crystalline product which upon recrystallization from acetone–methanol gave colorless crystals of mp 128.5 °C. The product was identified as iminosulfonium *p*-toluenesulfonic acid salt (III) by the following physical and chemical properties. Anal. Calcd for $C_{19}H_{19}NO_3S_2$: C, 60.45; H, 5.07; N, 3.71. Found: C, 60.83; H, 5.21; N, 3.48.

The salt III was then dissolved in chloroform again and washed with 20% aqueous alkali solution. After the chloroform layer was washed with water and the solution was dried, the solvent was evaporated to obtain a white, crystalline material in 75% yield which was recrystallized from benzene or benzene–hexane, mp 70–71 °C. This compound was identified as the free sulfilimine monohydrate. This sulfilimine (0.077 g) and *p*-toluenesulfonic acid (0.067 g) were dissolved in a drop of methanol and acetone was added to this solution. The melting point (128.5 °C) and ir spectrum were identical with those of the original salt III.

Method B. Diphenyl-*N*-*p*-tosylsulfilimine (25 g, 0.07 mol) was dissolved in 40 ml of 95% sulfuric acid. As soon as all the sulfilimine was dissolved, the solution was poured onto ice, made alkaline with aqueous sodium hydroxide solution, and then extracted with chloroform. Chloroform was evaporated at reduced pressure. The residue was dissolved again in 180 ml of 3% sulfuric acid. The solution was decolorized by charcoal. Then the solution was made alkaline. The crystalline precipitates were collected by filtration. Thus, diphenylsulfilimine (14 g) was obtained (90%).

Similarly the following sulfilimines were prepared.[27]

Phenyl-*p*-tolylsulfilimine: mp 54.5–55.5 °C; (KBr) 3170, 930 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.8 (m, 9 H, phenyl H), 2.40 (s, 3 H, CH_3), 1.7 ppm (s, 1 H, NH). Anal. Calcd for $C_{13}H_{13}NS$: C, 72.52; H, 6.08; N, 6.51. Found: C, 71.69; H, 6.19; N, 6.71.

Phenyl-*o*-tolylsulfilimine: mp 83.5–84.5 °C; (KBr) 3170, 930 cm^{-1}; NMR ($CDCl_3$) δ 7.1–7.8 (m, 9 H, phenyl H), 2.39 (s, 3 H, CH_3), 1.35 ppm (s, 1 H, NH). Anal. Calcd for $C_{13}H_{13}NS$: C, 72.52; H, 6.08; N, 6.51. Found: C, 73.16; H, 6.19; N, 6.21.

Phenyl-*p*-chlorophenylsulfilimine: mp 48–49 °C; ir (KBr) 3140, 935 cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.7 (m, 9 H, phenyl), 1.4 ppm (s, 1 H, NH). Anal. Calcd for $C_{12}H_{10}NCl$: C, 61.14; H, 4.28; N, 5.94. Found: C, 61.02; H, 4.33; N, 5.92.

Phenyl-*m*-chlorophenylsulfilimine: mp 35–36 °C; ir (KBr) 3110, 940 cm^{-1}; NMR ($CDCl_3$) δ 7.3–7.7 (m, 9 H, phenyl), 2.0 ppm (s, 1 H, NH). Anal. Calcd for $C_{12}H_{10}NCl$: C, 61.14; H, 4.28; N, 5.94. Found: C, 60.67; H, 4.46; N, 6.17.

Phenyl-*p*-nitrophenylsulfilimine: mp 98–99 °C; ir (KBr) 3150, 940 cm^{-1}; NMR ($CDCl_3$) δ 7.4–8.4 (m, 9 H, phenyl), 2.1 ppm (1 H, NH). Anal. Calcd for $C_{12}H_{10}O_2N_2S$: C, 58.52; H, 4.09; N, 11.37. Found: C, 58.53; H, 4.20; N, 11.17.

Phenyl-*o*-nitrophenylsulfilimine: mp 104–104.5 °C; ir (KBr) 3110, 960 cm^{-1}; NMR ($CDCl_3$) δ 7.2–8.6 (m, 9 H, phenyl), 1.8 ppm (s, 1 H, NH). Anal. Calcd for $C_{12}H_{10}O_2N_2S$: C, 58.52; H, 4.09; N, 11.37. Found: C, 58.67; H, 4.15; N, 11.38.

Methyl-*p*-tolylsulfilimine (Picrate): mp 158–159 °C. Anal. Calcd for $C_{14}H_{14}O_7N_4S$: C, 43.98; H, 3.69; N, 14.65. Found: C, 43.54; H, 3.61; N, 14.37.

Cyclopropyl-*p*-tolylsulfilimine (Picrate): mp 138–139 °C. Anal. Calcd for $C_{16}H_{16}O_7N_4S$: C, 47.06; H, 3.95; N, 13.72. Found: C, 47.35; H, 3.67; N, 13.62.

Pentamethylenesulfilimine (Picrate): mp 191 °C. Anal. Calcd for $C_{11}H_{14}O_7N_4S$: C, 38.15; H, 4.07; N, 16.18. Found: C, 38.22; H, 4.00; N, 16.21.

Methylphenylsulfilimine. The *N*-*p*-tosylsulfilimine (1 g, 0.34 mmol) was dissolved into 2 ml of 95% sulfuric acid. The reaction mixture was poured into well-cooled ethyl ether and immediately formed an oily material, i.e., the sulfuric acid salt of the free sulfilimine from which the free sulfilimine was obtained upon treatment of acetone–methanol solution of the salt with liquid ammonia. The free methyl-*N*-phenylsulfilimine is an oily substance and unstable at room temperature; therefore it was converted to picrate. The picrate was recrystallized from water, mp 112–112.5 °C. Anal. Calcd for $C_{13}H_{12}O_6N_4S$: C, 42.39; H, 3.28; N, 15.21. Found: C, 42.25; H, 3.15; N, 15.29. Besides this, 0.36 g (55%) of *p*-toluenesulfonic acid was isolated from the ether layer.

Reaction of Diphenylsulfilimine with *p*-Tosyl Chloride. Diphenylsulfilimine (0.10 g, 0.5 mmol) and *p*-tosyl chloride (0.10 g) were dissolved in 1 ml of pyridine. After 10 min the solution was poured onto cold water. The aqueous solution was extracted with chloroform, washed with water, and dried over sodium sulfate. After chloroform was removed, the residue was recrystallized from methanol; *N*-*p*-tosylsulfilimine (0.12 g) was obtained in 70% yield, mp 111 °C.

Acidic Hydrolysis of Diphenylsulfilimine. Diphenylsulfilimine (0.20 g, 1 mmol) was dissolved in 1 ml of 20% aqueous sulfuric acid. This solution was heated at 65–70 °C for 3 h and then was cooled at room temperature and extracted with chloroform. The chloroform solution was washed with water and dried over sodium sulfate and chloroform was removed. Diphenyl sulfoxide (0.18 g, 97%) was obtained.

Meanwhile, diphenylsulfilimine (0.20 g) was dissolved in 5 ml of methanol and 5 ml of aqueous 20% sodium hydroxide was added into this solution. The mixture was refluxed for 24 h; however, diphenylsulfilimine was recovered completely.

Pyrolysis of Sulfilimine. Diphenylsulfilimine (0.20 g, 1.0 mmol) was heated at 100 °C in a sealed tube for 6 h. After the reaction, a gaseous product was found to be ammonia which was dissolved in water and identified by Nessler's reagent. The oily material obtained was identified as diphenyl sulfide by ir and GLC.

ESR Measurement. ESR measurements of diphenyl-, phenyl-*p*-tolyl-, and *p*-nitrophenylphenyl-*N*-*p*-tosylsulfilimines were attempted in 95% sulfuric acid. However, no signals were observed.

Oxidation of Sulfilimine by Potassium Permanganate. Diphenylsulfilimine (0.20 g, 1.0 mmol) was dissolved in 15 ml of methanol. To this solution was added 0.5 g of potassium permanganate in 5 ml of water. The suspension was refluxed for 1 h with stirring and the inorganic precipitates were filtered off. After the solvent was evaporated, diphenylsulfoximine was obtained, 0.21 g (100%). Recrystallization from benzene gave a pure compound: mp 104 °C; ir (KBr) 3270 (NH), 1230, 1130, 1095, 980, 965 cm^{-1} (NSO). Other sulfoximines were prepared similarly by treating the corresponding free sulfilimines with potassium permanganate.

Oxidation of Diphenylsulfilimine by *p*-Methylperbenzoic Acid. Diphenylsulfilimine (0.20 g, 1.0 mmol) in 5 ml of methanol was added to 0.15 g of perbenzoic acid in 5 ml of methanol. The solution was kept at room temperature for 24 h until the TLC spot of the free sulfilimine disappeared. The solution was poured into an aqueous alkaline solution and the aqueous solution was extracted with chloroform. The chloroform solution was dried over anhydrous sodium sulfate. After the solvent was removed, an oily material formed, which was chromatographed through a column packed with silica gel. Then diphenylsulfoximine and diphenyl sulfone were obtained in 40 and 20% yield, respectively.

Preparation of Diphenyl-*N*-acylsulfilimine. Diphenyl-*N*-acetylsulfilimine. Diphenylsulfilimine (0.20 g, 1.0 mmol) was dissolved into 5 ml of benzene. To this solution, acetic anhydride (excess) was added at room temperature. After 10 min the benzene solution was washed with water and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residual oil solidified to white crystals which were recrystallized from ethanol. The yield was 0.22 g (95%): mp 89 °C; ir (KBr) 1575, 1590, 800 cm^{-1}. Anal. Calcd for $C_{14}H_{13}ONS$: C, 69.17; H, 5.35; N, 5.62. Found: C, 69.10; H, 5.38; N, 5.72.

Diphenyl-*N*-benzoylsulfilimine. Treatment of diphenylsulfilimine (0.20 g, 1.0 mmol) with an equimolar amount of benzoyl anhydride under the same reaction condition as above afforded diphenyl-*N*-benzoylsulfilimine in 95% yield: mp 126–127 °C; ir (KBr) 1595, 1550, 805 cm^{-1}. Anal. Calcd for $C_{19}H_{15}ONS$: C, 74.72; H, 4.95; N, 4.95. Found: C, 74.67; H, 4.95; N, 4.54.

***p*-Nitrophenyl-*N*-acetylphenylsulfilimine.** The reaction condition was similar to the above. Yield was 95%: mp 104 °C; ir (KBr) 1610, 1570, 1000 cm^{-1}. Anal. Calcd for $C_{14}H_{12}O_3N_2S$: C, 57.72; H, 4.20; N, 9.72. Found: C, 57.70; H, 3.91; N, 9.16.

Diphenyl-*N*-phthalylsulfilimine. Treatment of diphenylsulfilimine (0.50 g, 2.5 mmol) with phthalic anhydride (0.37 g) under the same reaction condition afforded diphenyl-*N*-phthalylsulfilimine in 95% yield: mp 157–157.5 °C; ir (KBr) 1730, 1580, 1530, 815 cm^{-1}; NMR ($CDCl_3$) δ 7.5–8.0 (m, 10 H, phenyl), 8.4–8.7 ppm (m, 2 H, phenyl). Anal. Calcd for $C_{20}H_{15}O_3NS$: C, 68.75; H, 4.33; N, 4.01. Found: C, 68.60; H, 4.33; N, 3.94.

Diphenyl-*N*-succinylsulfilimine. The reaction condition was similar to the above: yield 88%; mp 130–131 °C; ir (KBr) 1730, 1608, 1580, 810 cm^{-1}; NMR ($CDCl_3$) τ 7.5–8.0 (m, 10 H, phenyl), 6.35, 6.80 (dd, 2 H, –CH=CH–). Anal. Calcd for $C_{16}H_{15}O_3NS$: C, 64.20; H, 4.38; N, 4.68. Found: C, 64.26; H, 4.39; N, 4.54.

Diphenyl-*N*-ethylcarboethoxysulfilimine. Diphenylsulfilimine (0.5 g, 2.5 mmol) was dissolved into 5 ml of benzene. To this solution, ethyl chloroformate (0.27 g) was added at room temperature. The solution was kept standing for 1 h. Then the benzene solution was washed with water and dried over magnesium sulfate. After the solvent was evaporated, an oily residue solidified. Diphenyl-*N*-ethylcarboethoxysulfilimine was thus obtained, 0.67 g (89%). The crude crystals were recrystallized from ethanol: mp 91–92 °C; ir (KBr) 1610, 1570, 825 cm^{-1}. Anal. Calcd for $C_{15}H_{15}O_2NS$: C, 65.91; H, 5.53; N, 5.12. Found: C, 66.02; H, 5.52; N, 5.12.

Diphenyl-*N*-(*N'*-ethylcarbamoyl)sulfilimine. The treatment of diphenylsulfilimine with ethyl isocyanate in benzene solution at room temperature afforded diphenyl-*N*-(*N'*-ethylcarbamoyl)sulfilimine in 95% yield: mp 87 °C; ir (KBr) 1605, 1580 cm^{-1}; NMR ($CDCl_3$) 7.3–7.8 (m, 10 H, phenyl), 3.25 (q, 2 H, $-CH_2-$), 1.13 (t, 3 H, CH_3).

Diphenyl-*N*-(*N'*-phenylcarbamoyl)sulfilimine. The sulfilimine was obtained in 95% yield: mp 124–126 °C; ir (KBr) 1608, 1505, 808 cm^{-1}. Anal. Calcd for $C_{19}H_{16}ON_2S$: C, 71.22; H, 5.03; N, 8.74. Found: C, 71.44; H, 5.04; N, 8.85.

Diphenyl-*N*-(*N'*-phenylthiocarbamoyl)sulfilimine. Treatment of sulfilimine with phenyl thioisocyanate under similar conditions as above afforded the sulfilimine in 95% yield: mp 138.5 °C (CH_3Cl–acetone); ir (KBr) 970 cm^{-1}. Anal. Calcd for $C_{19}H_{16}N_2S_2$: C, 67.82; H, 4.79; N, 8.33. Found: C, 67.74; H, 4.77; N, 8.41.

Diphenyl-*N*-(δ-hydroxyvaleroyl)sulfilimine. A mixture of diphenylsulfilimine (1.00 g, 5 mmol) and 1.5 ml of δ-valerolactone in 10 ml of benzene was refluxed for 24 h until the TLC spot of the corresponding free sulfilimine disappeared. After benzene was evaporated, the residual oily material was chromatographed through a silica gel column using chloroform as an eluent. Thus, diphenyl-*N*-(δ-hydroxyvaleroyl)sulfilimine was obtained: 0.69 g (51%); mp 97–99 °C; ir (KBr) 1580, 1560, 805 cm^{-1}; NMR ($CDCl_3$) δ 7.3–8.0 (m, 10 H, phenyl), 3.6–4.2 (m, 2 H, OH + –CH–), 2.72 (t, 2 H, $-COCH_2CH_2CH-$), 1.90 (t, 2 H, $-COCH_2CH_2CH-$), 1.20 (d, 3 H, CH_3). Anal. Calcd for $C_{17}H_{19}O_2NS$: C, 67.75; N, 6.35; N, 4.65. Found: C, 67.74; H, 6.36; N, 4.60.

Diphenyl-*N*-acetoacetylsulfilimine. Diphenylsulfilimine (0.50 g, 2.5 mmol) was dissolved in 5 ml of benzene. To this solution was added freshly distilled ketene dimer cooling in an ice–water bath. Then benzene was evaporated and a crystalline residue was obtained, 0.60 g (75%). The crude crystals were recrystallized from ethanol–ether: mp 67–68.5 °C; ir (KBr) 1700, 1590, 1570 cm^{-1}; NMR ($CDCl_3$) δ 7.4–8.0 (m, 10 H, phenyl), 3.55 (s, 2 H, CH_2), 2.26 (s, 3 H, CH_3). Anal. Calcd for $C_{16}H_{15}O_2NS$: C, 67.34; H, 5.30; N, 4.91. Found: C, 67.46; H, 5.25; N, 4.78.

Reaction with Phenyl Thiobenzoate. Diphenylsulfilimine (0.50 g, 2.5 mmol) was dissolved in 10 ml of benzene. To this was added phenyl thiobenzoate (0.80 g) under cooling in an ice–water bath. After the addition, the solution was kept at room temperature for 1 h. The benzene solution was washed with dilute sodium hydroxide solution and dried over magnesium sulfate. Benzene was removed affording 0.41 g of diphenyl-*N*-benzoylsulfilimine in 60% yield, mp 127 °C.

Reaction with Ethyl Acetoacetate. Diphenylsulfilimine (0.40 g, 2.0 mmol) was mixed with 1 ml of ethyl acetoacetate in 10 ml of benzene. The solution was refluxed for 24 h. Then benzene was evaporated and the residue was separated through a chromatography column of silica gel using chloroform as an eluent. After the solvent was evaporated, *N*-acetoacetylsulfilimine was obtained, 0.22 g (40%), as an oil.

Registry No.—I (R = R' = C_6H_5), 13150-76-0; I (R = *p*-$CH_3C_6H_4$; R = C_6H_5), 24702-37-2; I (R = *o*-$CH_3C_6H_4$; R = C_6H_5), 53897-89-5; I (R = *p*-ClC_6H_4; R' = C_6H_5), 24702-38-3; I (R = *m*-ClC_6H_4; R' = C_6H_5), 58463-51-7; I (R = *p*-$NO_2C_6H_4$; R' = C_6H_5), 24698-06-4; I (R = *o*-$NO_2C_6H_4$; R' = C_6H_5), 58463-52-8; I (R = CH_3; R' = *p*-$CH_3C_6H_4$), 24702-26-9; I (R = c-C_3H_5; R' = *p*-$CH_3C_6H_4$), 58463-53-9; I (R,R' = $-(CH_2)_5-$), 13553-73-6; I (R = CH_3; R' = C_6H_5), 10330-22-0; II (R = R' = C_6H_5), 36744-90-8; II (R = *p*-$CH_3C_6H_4$; R' = C_6H_5), 36744-92-0; II (R = *o*-$CH_3C_6H_4$; R' = C_6H_5), 54615-60-0; II (R = *p*-ClC_6H_4; R' = C_6H_5), 36744-94-2; II (R = *m*-ClC_6H_4; R' = C_6H_5), 58463-54-0; II (R = *p*-$NO_2C_6H_4$; R' = C_6H_5), 36744-95-3; II (R = *o*-$NO_2C_6H_4$, R' = C_6H_5), 54615-61-1; II (R = CH_3; R' = *p*-$CH_3C_6H_4$) picrate, 58463-56-2; II (R = c-C_3H_5; R' = *p*-$CH_3C_6H_4$) picrate, 58463-58-4; II (R,R' = $-(CH_2)_5-$) picrate, 58463-59-5; II (R = CH_3; R' = C_6H_5) picrate, 58463-60-8; III, 58463-61-9; sulfuric acid, 7664-93-9; *p*-tosyl chloride, 98-59-9; potassium permanganate, 7722-64-7; diphenylsulfoximine, 22731-83-5; *p*-methylperbenzoic acid, 937-21-3; diphenyl-*N*-acetylsulfilimine, 42397-41-1; diphenyl-*N*-benzoylsulfilimine, 39149-60-5; benzoyl anhydride, 93-97-0; *p*-nitrophenyl-*N*-acetylphenylsulfilimine, 58463-62-0; diphenyl-*N*-phthalylsulfilimine, 58463-63-1; diphenyl-*N*-succinylsulfilimine, 58485-81-7; diphenyl-*N*-ethylcarboethoxysulfilimine, 39149-62-7; ethyl chloroformate, 541-41-3; diphenyl-*N*-(*N'*-ethylcarbamoyl)sulfilimine, 58463-64-2; ethyl isocyanate, 109-90-0; diphenyl-*N*-(*N'*-phenylcarbamoyl)sulfilimine, 42397-43-3; diphenyl-*N*-(*N'*-phenylthiocarbamoyl)sulfilimine, 58463-65-3; phenyl thioisocyanate, 103-72-0; diphenyl-*N*-(δ-hydroxyvaleroyl)sulfilimine, 58463-66-4; δ-valerolactone, 542-28-9; diphenyl-*N*-acetoacetylsulfilimine, 58463-67-5; phenyl thiobenzoate, 884-09-3; ethyl acetoacetate, 141-97-9.

References and Notes

(1) Free Sulfilimines. 5. Part 4: ref 13.
(2) (a) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schrilts, D. J. Duchamp, and D. C. Garwood, *J. Am. Chem. Soc.*, **92**, 7369 (1970); (b) B. H. Nicolet and J. Willard, *Science*, **53**, 217 (1921); (c) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 1052 (1922).
(3) I. Kapovits, F. Ruff, and A. Kucsmann, *Tetrahedron*, **28**, 4405, 4413 (1972).
(4) N. Furukawa, T. Omata, T. Yoshimura, T. Aida, and S. Oae, *Tetrahedron Lett.*, 1619 (1972).
(5) R. A. Appel, W. Buchner, and E. Guth, *Justus Liebigs Ann. Chem.*, **618**, 53 (1958); *Angew. Chem.*, **71**, 701 (1959); *Chem. Ber.*, **95**, 849, 855, 2220 (1962).
(6) (a) J. B. Lambert, C. E. Mixan, and O. S. Bailey, *Chem. Commun.*, 316 (1971); (b) J. B. Lambert, C. E. Mixan, and D. S. Bailey, *J. Am. Chem. Soc.*, **94**, 208 (1972).
(7) Y. Tamura, K. Sumoto, J. Minamikawa, and M. Ikeda, *Tetrahedron Lett.*, 4137 (1972).

(8) J. A. Franz and J. C. Martin, *J. Am. Chem. Soc.*, **97**, 583 (1975).
(9) N. Kunieda and S. Oae, *Bull. Chem. Soc. Jpn.*, **46**, 1745 (1973).
(10) H. R. Bentley, and J. K. Whitehead, *J. Chem. Soc.*, 2081 (1950).
(11) N. Furukawa, T. Omata, and S. Oae, *Chem. Commun.*, 590 (1973).
(12) (a) A. Fava, P. B. Sogs, and M. Calvin, *J. Am. Chem. Soc.*, **79**, 1078 (1957); (b) H. J. Shine and L. Piette, *ibid.*, **84**, 4798 (1962); (c) S. Oae and N. Kunieda, *Bull. Chem. Soc. Jpn.*, **41**, 696 (1968).
(13) N. Furukawa, T. Yoshimura, T. Omata, and S. Oae, *Chem. Ind. (London)*, 702 (1974).
(14) (a) A. Kucsman, I. Kapovits, and F. Ruff, *Acta Chim. Acad. Sci. Hung.*, **40**, 75 (1964); (b) *Tetrahedron*, **22**, 1575, 1843 (1966); (c) S. Kucsman, F. Ruff, and I. Kapovits, *Acta Chim. Acad. Sci. Hung.*, **50**, 325 (1966); (d) A. Kalman, *Acta Crystallogr.*, **22**, 501 (1967); (e) K. Tsujihara, N. Furukawa, and S. Oae, *Bull. Chem. Soc. Jpn.*, **43**, 2153 (1970).
(15) Appel et al. claimed the formation of free nitrene which disproportionates to ammonia and nitrogen gas.
(16) W. Lwowski, Ed., "Nitrenes", Wiley, New York, N.Y., 1970.
(17) (a) L. Reiner and F. Flodalisi, U.S. Patent 2 648 705 (1953); (b) J. S. Berry, French Patent 1 377 794 (1964); U.S. Patent 3 255 116 (1966); (c) F. Misani, T. W. Fair, and L. Reiner, *J. Am. Chem. Soc.*, **73**, 459 (1951); (d) H. R. Bentley, E. E. McDermott, and J. K. Whitehead, *Proc. R. Soc. London, Ser. B*, **138**, 262 (1951); (e) J. K. Whitehead and H. R. Bentley, *J. Chem. Soc.*, 1572 (1952); (f) D. Jerchel, L. Dippelhofer, and D. Renner, *Chem. Ber.*, **87**, 947 (1954); (g) K. Hayashi, *Chem. Pharm. Bull.*, **8**, 177 (1960).
(18) (a) L. Horner and A. Christman, *Chem. Ber.*, **96**, 388 (1963); (b) L. Horner, G. Bauer, and J. Doerges, *ibid.*, **98**, 2631 (1965); (c) H. Kwart and A. A. Kahn, *J. Am. Chem. Soc.*, **89**, 1950 (1967).
(19) (a) D. Carr, T. P. Sesen, and R. Q. Turner, *Tetrahedron Lett.*, 477 (1969); (b) C. R. Johnson, R. A. Kirchhoff, R. J. Reisher, and G. F. Katekar, *J. Am. Chem. Soc.*, **95**, 4287 (1973); (c) M. Moriyama, T. Numata, and S. Oae, *Org. Prep. Proced. Int.*, **6**, 207 (1974).
(20) S. Oae, K. Harada, K. Tsujihara, and N. Furukawa, *Int. J. Sulfur Chem., Part A*, **2**, 49 (1972).
(21) H. J. Shine and J. J. Silber, *J. Am. Chem. Soc.*, **94**, 1026 (1972).
(22) Y. Tamura, K. Sumoto, H. Matushima, H. Taniguchi, and M. Ikeda, *J. Org. Chem.*, **38**, 4324 (1973).
(23) S. Oae, T. Masuda, K. Tsujihara, and N. Furukawa, *Bull. Chem. Soc. Jpn.*, **45**, 3586 (1972).
(24) Ordinarily esters such as ethyl acetate or ethyl benzoate did not react with free sulfillimine under the present reaction condition.
(25) K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Jpn.*, **42**, 2631 (1969).
(26) N. Furukawa, T. Yoshimura, and S. Oae, unpublished result.
(27) All sulfilimines thus obtained have crystalline water but the content of it is not so clear so that some slightly erroneous elemental analyses data were obtained.

Synthesis of [1]Benzothieno[3,2-*d*]-*v*-triazine Derivatives. A Unique Diazonium Ion Cyclization

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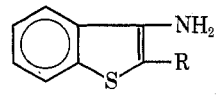
Received December 9, 1975

Diazotization of 3-aminobenzo[*b*]thiophene-2-carbonitrile in hydrochloric acid yielded 4-chloro[1]benzothieno-[3,2-*d*]-*v*-triazine. Various derivatives were prepared by nucleophilic displacement using methoxide, methylamine, dimethylamine, hydrazine, and hydroxide ion. The parent heterocycle, [1]benzothieno[3,2-*d*]-*v*-triazine, was obtained by oxidation of the hydrazine derivative.

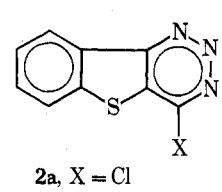
Diazonium ion condensation with an adjacent nucleophilic function to form a five- or six-membered ring has proved valuable for synthesizing various nitrogen heterocycles. Among these are numerous 1,2,3-benzotriazines, including 4-ones from carboxamides,[1] 4-imines from amidines,[2] 3-amino-4-ones from carboxhydrazides,[3] 3-oxides from oximes,[4] and 4-amino-3-oxides from amidoximes.[5] Other examples involving cyclization with nitrogen nucleophiles include the preparation of benzothiatriazine *S,S*-dioxides from sulfonamides[6] and benzotriazoles from amines.[7] Examples of cyclization with carbon nucleophiles are the synthesis of 4-cinnolones from ketones[8] and nitroindazoles from activated methyl functions.[9] Indazole itself has been prepared in high yield from diazotized *o*-toluidine.[10]

We were unable to find any examples in the literature that involved condensation of a diazonium ion with an adjacent cyano function. Therefore, we were surprised when the product obtained by diazotization of 3-aminobenzo[*b*]thiophene-2-carbonitrile (**1a**)[11] in hydrochloric acid was 4-chloro[1]benzothieno[3,2-*d*]-*v*-triazine (**2a**, 77% yield). The product underwent normal halide displacement with a variety of nucleophiles, including methoxide ion, methylamine, dimethylamine, and hydrazine, to yield the derivatives **2b** (87%), **2c** (70%), **2d** (63%), and **2e** (55%), respectively. Complex mixtures were obtained with ammonia, azide, and excess methyl mercaptan anion, indicating possible triazine ring fission with these nucleophiles. Oxidation of the hydrazine derivative **2e** with mercuric oxide[12] yielded the parent heterocycle **2f** (54%). The ultraviolet spectrum of **2f** was similar to that of **2a** (see Experimental Section).

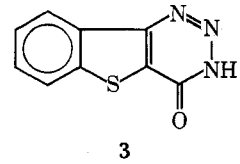
An unequivocal synthesis of **2a** was attempted by, first of all, hydrolyzing **1a** in alcoholic potassium hydroxide to form the carboxamide **1b** (82%). Diazotization of **1b** in sulfuric acid yielded the triazinone **3** (88%).[13] Attempts to prepare **2a** from **3** utilizing standard reagents (phosphorus oxychloride, phosphorus trichloride, and thionyl chloride–DMF) were unsuccessful, apparently owing to the instability of the triazine ring. Nevertheless, a proof of structure was accomplished by treating **2a** with aqueous potassium hydroxide and obtaining a triazinone (79%) identical in all respects with **3**. When **3** was subjected to the same reaction conditions utilized in the formation of **2a** from **1a**, it was recovered unchanged, indicating that it is not an intermediate in that transformation.



1a, R = CN
b, R = $CONH_2$



2a, X = Cl
b, X = OCH_3
c, X = $NHCH_3$
d, X = $N(CH_3)_2$
e, X = $NHNH_2$
f, X = H



3

The scope of this interesting triazine ring closure will receive our further attention. No evidence for the presence of 4-chloro-1,2,3-benzotriazine was found when anthranilonitrile