E. Ochiai, "Aromatic Amine Oxides", Elsevier, Amsterdam, 1967, p 178.
(3) Preliminary communication: R. A. Abramovitch, S. Kato, and G. M. Singer, *J. Am. Chem. Soc.*, **93**, 3074 (1971).
(4) A. R. Katritzky and E. Lunt, *Tetrahedron*, **25**, 4291 (1969).
(5) R. A. Abramovitch and J. G. Saha, *Tetrahedron*, **21**, 3297 (1965). R. A. Abramovitch and O. A. Koleoso, *J. Chem. Soc. B*, 1292 (1968).
(6) R. A. Abramovitch and G. M. Singer, *J. Am. Chem. Soc.*, **91**, 5672 (1969); *J. Org. Chem.*, **39**, 1795 (1974).
(7) H. Zollinger, *Acc. Chem. Res.*, **6**, 335 (1973).
(8) R. A. Abramovitch, G. M. Singer, and A. R. Vinutha, *Chem. Commun.*, 55 (1967); R. A. Abramovitch and A. R. Vinutha, *J. Chem. Soc. B*, 131 (1971); J. A. Zoltewicz and L. S. Helmick, *J. Am. Chem. Soc.*, **92**, 7547 (1970).
(9) J. W. Haworth, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 358 (1940).
(10) V. Sneickus and G. Kan, *J. Chem. Soc., Chem. Commun.*, 172 (1972).
(11) C. W. Bird and M. A. Sheikh, *Tetrahedron Lett.*, 1333 (1975).
(12) T. Okamoto, S. Hayashi, H. Horikiri, and M. Hirobe, *Yakagaku Zasshi*, **91**, 210 (1971); *Chem. Abstr.*, **74**, 99818k (1971).
(13) a. H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Chem. Ber.*, **89**, 209 (1956); H. Meerwein, P. Laasch, R. Mersch, and J. Nentwig, *Ibid.*, **89**, 224 (1956); (b) T. Okamoto and S. Hayashi, *Yakugaku Zasshi*, **86**, 766 (1966); *Chem. Abstr.*, **65**, 20116*h* (1966).
(14) R. A. Damico, U.S. Patent 3 590 035 (1971); *Chem. Abstr.*, **75**, 63616z (1971).
(15) A. Roe, *Org. React.*, **5**, 193 (1949).
(16) P. E. Verkade, C. P. vanDijk, and W. Meerburg, *Recl. Trav. Chim. Pays-Bas*, **65**, 346 (1946).
(17) M. C. Sendel, K. L. Viste, and R. Y. Yih, German Offen. 1 900 947 (1969); *Chem. Abstr.*, **72**, 21616g (1970).

Mesoionic Compounds. 38. The *anhydro*-2-Aryl-1,3-dithiolium Hydroxide System[1]

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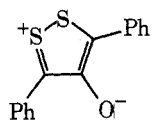
anhydro-4-Hydroxy-2-phenyl-1,3-dithiolium hydroxide has been prepared from thiobenzoylthioglycollic acid, acetic anhydride, and triethylamine at 0–10 °C and the product previously assigned this structure shown to be *anhydro*-4-hydroxy-2-phenyl-5-(thiobenzoylthiomethylcarbonyl)-1,3-dithiolium hydroxide. This mesoionic ring system undergoes ready cycloaddition of acetylenic dipolarophiles yielding substituted thiophenes with elimination of carbonyl sulfide. With olefinic dipolarophiles and azirines stable 1:1 adducts were formed.

Interest in the chemistry of five-membered ring systems containing sulfur has increased considerably over the past several years, particular attention being paid to those systems containing two sulfur atoms in the 1,2 positions[2] and in the 1,3 positions.[3] Cycloaddition reactions have played a prominent part in these studies,[4] and have resulted in several useful synthetic procedures. Mesoionic derivatives[5] of both the 1,2-dithiole and 1,3-dithiole ring systems can be devised and a study of their synthesis and properties was initiated as part of our interests in this area.

anhydro-3,5-Diphenyl-4-hydroxy-1,2-dithiolium hydroxide (**1**) has been synthesized[6] from 1,1,3,3-tetrabromo-1,3-diphenylacetone and potassium ethyl xanthate, or from 1,3-diphenylpropanetrione and H_2S–HCl, followed by Et_3N.[7] We have found this ring system to be completely unresponsive to a variety of dipolarophiles[8] whereas *anhydro*-4-hydroxy-2-phenyl-1,3-dithiolium hydroxide (**2**, R = Ph; R^1 = H) was an extremely reactive system whose reactions are described below.



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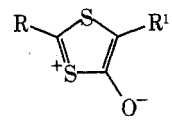


2

3

The ring system **2** was described as being prepared from thiobenzoylthioglycollic acid (**3**, R = Ph; R^1 = H) and acetic anhydride–boron trifluoride.[9a] The corresponding exocyclic imino derivatives have also been prepared by cyclization of cyanomethyl dithiobenzoate with anhydrous HCl or acid chlorides,[9b] and an unstable ortho-protonated derivative of **2** (R = Ph; R^1 = H) was obtained by cyclization of carboxymethyl dithiobenzoate with perchloric acid,[9c] a convenient cyclization agent for the preparation of a variety of 1,3-dithioles.[3]

Repetition of the reported procedure[9a] gave a deep-red, crystalline product, mp 185–186 °C dec, as described previously when a reaction time of several minutes was used. Longer reaction times resulted in considerable polymer formation. This red product failed to undergo cycloadditions with several dipolarophiles and, on examination of its spectral characteristics, they were found to be incompatible with the assigned structure. The mass spectrum showed an ion at *m/e* 388 (5%), most likely a molecular ion which, in conjunction with analytical data, established the molecular formula as $C_{18}H_{12}O_2S_4$. The NMR data for this product indicated the presence of two phenyl groups [δ 7.48 (m, 10)] and two methylene protons which appeared as two AB doublets (J = 16.5 Hz) at δ 4.33–4.08 and 4.01–3.75, and the infrared spectrum showed two absorptions at 1690 and 1590 cm^{-1}, conceivably due to two carbonyl groups related to each other in such a way that an exocyclic negative charge was delocalized over both groups. These data are most satisfactorily accommodated by the structure *anhydro*-4-hydroxy-2-phenyl-5-(thiobenzoylthiomethylcarbonyl)-1,3-dithiolium hydroxide (**2**, R = Ph; R^1 = $COCH_2SCSPh$).

This "overacylation" of a mesoionic system under similar cyclodehydration conditions has been observed in the oxazole,[10] imidazole,[11] and thiazole[12] ring systems, and the spectral parameters of this present product are consistent with those of the comparable products in these ring systems. Indicative of a high degree of charge density at that position of the nucleus, it also indicates considerable potential in 1,3-dipolar cycloaddition reactions. However, these acylated products themselves often do not undergo cycloadditions owing to delocalization of the negative charge of the masked 1,3-dipole over the carbonyl groups.

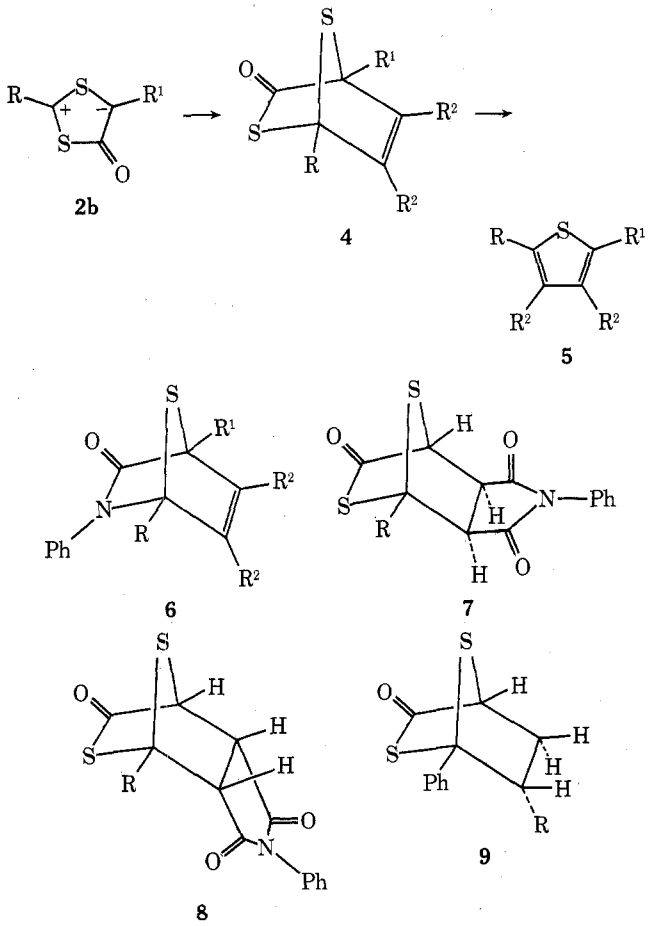
The acylation can often be avoided by the use of Et_3N and low reaction temperatures.[12c] When the thiobenzoylthioglycollic acid (**3**, R = Ph; R^1 = H) was treated with a mixture of Et_3N–Ac_2O (1:3) at 0–10 °C for several minutes only, glistening scarlet needles, mp 113–115 °C dec, were obtained. That this product was the desired mesoionic system, *anhydro*-4-hydroxy-2-phenyl-1,3-dithiolium hydroxide (**2**, R = Ph; R^1 = H) was evident from the following considerations. Analytical and mass spectral data [$M^{\cdot+}$ 194 (40%)] showed the molecular formula to be $C_9H_6S_2O$ and, in addition to aromatic protons at δ 7.51 (5), the NMR spectrum showed only a sharp

singlet at δ 6.06. This chemical shift, together with a ν_{CO} at 1610 cm^{-1}, is characteristic of mesoionic systems,[12c] and the correctness of this structural assignment was evident from the chemical transformations described below. The chemical shift δ 6.06 for the C_5 H should be compared with those of analogous protons in 1,3-dithiolium salts.[9c] In these salts the C_5 H usually falls in the range δ 8.73–4.92, depending on the 2 substituent, and the shift to a high field in this present system no doubt reflects the increased shielding at the C-5 position caused by delocalization of the exocyclic negative charge.

Use of *p*-chlorothiobenzoylthioglycollic acid (**3**, R = *p*-ClC_6H_4; R^1 = H) and *p*-methoxythiobenzoylthioglycollic acid (**3**, R = *p*-$CH_3OC_6H_4$; R^1 = H) in the above reaction gave the corresponding 2-*p*-chlorophenyl and 2-*p*-methoxyphenyl derivatives of **2**. These mesoionic compounds were moderately sensitive in solution to traces of moisture, undergoing hydrolysis to their precursors, and optimum results were obtained only by using very pure dithioglycollic acids and working under "drybox" conditions with anhydrous solvents. They are quite stable in the dry, solid state.

5-Phenyl and 5-methyl derivatives of **2** have also been prepared[13] by Ac_2O–Et_3N cyclization of the corresponding disubstituted thioglycollic acid. However, the additional substituent renders the reaction conditions far less critical than those employed for the synthesis of **2** (R = aryl; R^1 = H), a feature which has also been observed in the *anhydro*-4-hydroxy-2-phenylthiazolium hydroxide system.[14]

The ring system **2** contains a masked 1,3-dipole of the thiocarbonyl ylide type represented by **2b**. Dimethyl acetylenedicarboxylate added readily to **2** (R = Ph; R^1 = H) giving dimethyl 2-phenylthiophene-3,4-dicarboxylate (**5**, R = Ph; R^1 = H; R^2 = $COOCH_3$) in reasonable yield. The 2,7-dithiabicyclo[2.2.1]heptane **4** (R = Ph; R^1 = H; R^2 = $COOCH_3$) was the likely intermediate in the cycloaddition but elimination of carbonyl sulfide occurred so readily at 80 °C



2b **4** **5** **6** **7** **8** **9**

that **4** could not be isolated. Similar facile eliminations of carbonyl sulfide have been observed from the initial cycloadducts from *anhydro*-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide and acetylenic dipolarophiles.[12c] The 2-*p*-methoxyphenyl- and 2-*p*-chlorophenylthiophenes **5** (R = *p*-$CH_3OC_6H_4$ and *p*-ClC_6H_4; R^1 = H; R^2 = $COOCH_3$) were obtained readily from the corresponding substituted derivatives of **2** (R = *p*-$CH_3OC_6H_4$ and *p*-ClC_6H_4; R^1 = H). Similarly dibenzoylacetylene and **2** (R = Ph; R^1 = H) gave[15] the corresponding thiophene **5** (R = Ph; R^1 = H; R^2 = COPh). The structures of these thiophenes were readily established by analytical and spectral data (Experimental Section). Thus in **5** (R = Ph; R^1 = H; R^2 = $COOCH_3$) the NMR spectrum showed a singlet proton at δ 7.98, consistent with the 5 proton being deshielded by the 4-$COOCH_3$ substituent and shifted downfield from the usual chemical shift of δ 7.19 in thiophene.[16] The mass spectra of the thiophenes all showed molecular ions and fragmentation patterns consistent with the assigned structures.

It has also been shown[17] that the corresponding 5-aryl and 5-methyl derivatives of **2** (R = R^1 = aryl; R = aryl, R^1 = CH_3) undergo ready cycloaddition with similar acetylenic dipolarophiles yielding the appropriate thiophenes **5** (R = R^1 = aryl; R = aryl, R^1 = CH_3). Thus in conjunction with the *anhydro*-2,3,5-triaryl-4-hydroxythiazolium hydroxides,[14] the ring system **2** is a useful synthon for a variety of thiophenes not readily available by other routes.

N-Phenylmaleimide underwent ready reaction with **2** (R = Ph; R^1 = H) in refluxing benzene over 6 h. The product was shown to be a simple 1:1 cycloadduct of molecular formula $C_{19}H_{13}NO_3S_2$ from analytical and spectral data, the latter also allowing a choice between the exo adduct **7** (R = Ph) and the endo adduct **8** (R = Ph). A one-proton doublet of doublets (J = 6.6, 1.0 Hz) at δ 3.93 (H_5), a doublet (J = 6.6 Hz) at δ 4.29 (H_6), and a doublet at δ 4.88 (J = 1.0 Hz) are only compatible with the endo adduct **8** (R = Ph), these chemical shifts and coupling constants also being consistent with those observed in related adducts.[18–20] Similar endo adducts **8** (R = *p*-$CH_3OC_6H_4$, *p*-ClC_6H_4) were obtained from **2** (R = *p*-$CH_3OC_6H_4$, *p*-ClC_6H_4; R^1 = H) and *N*-phenylmaleimide, and their chemical shifts and coupling constants are described in the Experimental Section. The cycloadducts **8** did not show molecular ions in their mass spectra, an ion corresponding to (M − COS) being observed together with those resulting from further fragmentation of the system. In contrast the reaction of **2** (R = R^1 = Ph) and *N*-phenylmaleimide required xylene at 150 °C and in this case a mixture of the exo and endo adducts was obtained.[18]

Acrylonitrile and ethyl acrylate also give 1:1 adducts with **2** (R = Ph; R^1 = H). The adduct from the former was assigned structure **9** (R = CN) on the basis of coupling of the bridgehead proton (H_4) to two other protons, indicating that the cyano group is in the 6 position. The chemical shifts and coupling constants for $H_{5\alpha}$, $H_{5\beta}$, and $H_{6\alpha}$ (Experimental Section) show that the cyano group is in an endo configuration. Although the NMR spectrum of the ethyl acrylate adduct was similar in gross features to that of the acrylonitrile product suggesting an endo configuration for the ethoxycarbonyl group, the overlapping of the chemical shifts made it difficult to assign the configuration of this group with any degree of certainty.

The mesoionic system **2** (R = Ph; R^1 = H) failed to yield an isolable product with diphenylcyclopropenone and 3-methyl-2-phenylazirine owing to its decomposition in refluxing toluene over extended reaction periods. However its 2,5-diphenyl derivative is considerably more stable both thermally and to traces of moisture and has been reported[21] to give 2,3,5,6-tetraphenyl-4*H*-thiopyran-4-thione with diphenylcyclopropenethione. We have found that **2** (R = R^1 =

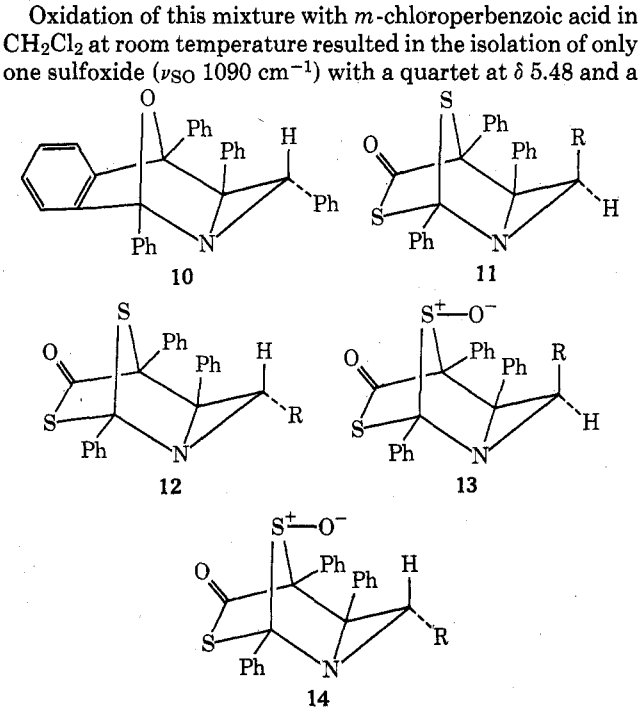
Ph) also reacts with azirines and in refluxing xylene with 2,3-diphenyl-1-azirine gave a multicomponent reaction mixture. The major product, isolated by chromatography (silica gel), was shown by its analytical and spectral data to be a 1:1 adduct. Earlier studies with 1-azirines in cycloadditions[22] suggest an addition of the "masked" ylide in **2** to the C=N of the azirine, with the possibility of some subsequent, skeletal rearrangement.

This thermally stable product (ν_{CO} 1690 cm^{-1}) had retained the skeletal arrangement of atoms present in the substrate **2** and its structure has been assigned in analogy with the structures of the products obtained[23] from 1,3-diphenylisobenzofuran and azirines and on the basis of the following spectral data and chemical reactions. Its NMR spectrum showed a singlet at δ 5.66 and a complex aromatic multiplet at δ 8.18–6.76. A second, minor isomeric product isolated from this reaction showed a singlet proton at δ 5.95 in addition to the aromatic multiplet. In the adduct **10**, the aziridine ring proton was observed at δ 4.52, being deshielded by the oxido bridge. This deshielding was helpful in establishing the structures of the adducts obtained above. Thus the major adduct was assigned structure **11** (R = Ph) with an endo aziridine proton (deshielding $\approx$ 2.14 ppm) and the minor adduct was assigned structure **12** (R = Ph) with an exo aziridine proton (deshielding $\approx$ 2.43 ppm). Oxidation of **11** (R = Ph) with 1 equiv of *m*-chloroperbenzoic acid in methylene chloride gave the corresponding sulfoxide **13** (R = Ph) (ν_{SO} 1077 cm^{-1}) whose aziridine proton had undergone only a small downfield shift (0.1 ppm) which would be anticipated for a proton in this configuration.

Two minor products were isolated in insufficient amounts for complete characterization from the initial cycloaddition and were thought to be 2,4,5-triphenylthiazole and 2,4,5-triphenyl-6*H*-1,3-thiazin-6-one on the basis of mass spectral fragmentation patterns.

3-Methyl-2-phenylazirine reacted with **2** (R = R^1 = Ph) in refluxing xylene over 11 h. The product isolated after chromatography (57%) was likewise identified as a 1:1 adduct (ν_{CO} 1680 cm^{-1}). Two quartets at δ 4.45 and 3.71 and two doublets at δ 1.35 and 1.11 demonstrated the presence of the two isomers **12** (R = CH_3) and **11** (R = CH_3), respectively in the ratio of 1:2.25. Attempts to separate this mixture by chromatography were unsuccessful.

Oxidation of this mixture with *m*-chloroperbenzoic acid in CH_2Cl_2 at room temperature resulted in the isolation of only one sulfoxide (ν_{SO} 1090 cm^{-1}) with a quartet at δ 5.48 and a doublet at δ 1.18. This downfield shift in the methine resonance (1.03 ppm) indicates that the isolated sulfoxide has structure **14** (R = CH_3), implying a syn relationship between the S–O group and the aziridine proton and hence derived from **12** (R = CH_3).



It is interesting that exo adducts only were isolated from azirines and the mesoionic system **2** whereas with olefinic dipolarophiles endo adducts were obtained. As in the adducts derived from 1,3-diphenylisobenzofuran,[23] this may be explained in terms of an unfavorable increase in energy for the endo transition state as a result of secondary orbital interactions. Although it was not possible to detect it experimentally, the initial formation of the endo adduct with a subsequent retro-1,3-dipolar reaction with the ultimate formation of the exo adduct cannot be excluded.

Experimental Section[24]

***anhydro*-4-Hydroxy-2-phenyl-1,3-dithiolium Hydroxide (2, R = Ph; R^1 = H).** Thiobenzoylthioglycollic acid[25] (2.5 g, 0.012 mol) was dissolved in a mixture of acetic anhydride (2 ml) and triethylamine (5 ml) at room temperature and the reaction mixture was cooled at 0 °C for 10 min, crystallization being induced by scratching the walls of the reaction vessel. Addition of anhydrous ether caused additional product to separate and this was collected and washed with anhydrous ether using "drybox" conditions throughout. The product of analytical purity was obtained as glistening scarlet needles: 1.75 g (77%); mp 113–115 °C dec; ir (KBr) 1610 cm^{-1} (CO); λ_{max} (anhydrous CH_3OH) 220 nm (log ϵ 4.24), 265 (3.96), 285 (3.89), and 325 (3.46); NMR ($CDCl_3$) δ 6.06 (s, 1, H_4), 7.51 (m, 5, aromatic); $M^{\cdot+}$ 194 (40).

Anal. Calcd for $C_9H_6OS_2$: C, 55.67; H, 3.12. Found: C, 55.55; H, 3.40.

Attempted recrystallization of the product always resulted in some ring opening occurring owing to traces of moisture present in the solvent.

Similarly *anhydro*-4-hydroxy-2-*p*-methoxyphenyl-1,3-dithiolium hydroxide (**2**, R = *p*-$CH_3OC_6H_4$; R^1 = H) was obtained from *p*-methoxythiobenzoylthioglycollic acid (**3**, R = *p*-$CH_3OC_6H_4$; R^1 = H) as brilliant, scarlet-red needles: 80%; mp 143–145 °C dec; ir (KBr) 1600 cm^{-1} (CO); λ_{max} (anhydrous CH_3OH) 230 nm (log ϵ 4.21), 255 (3.83), and 330 (3.83); NMR ($CDCl_3$) δ 3.88 (s, 3, OCH_3), 5.90 (s, 1, H_4), 6.88–7.03 (AB d, 2, J = 9.0 Hz, aromatic), 7.51–7.66 (AB d, 2, J = 9.0 Hz, aromatic); $M^{\cdot+}$ 224 (32).

Anal. Calcd for $C_{10}H_8O_2S_2$: C, 53.58; H, 3.60. Found: C, 53.80; H, 3.65.

anhydro-4-Hydroxy-2-*p*-chlorophenyl-1,3-dithiolium hydroxide (**2**, R = *p*-ClC_6H_4; R′ = H) also formed red needles, 75%, mp 160 °C dec.

Anal. Calcd for $C_9H_5ClOS_2$: C, 47.20; H, 2.19. Found: C, 47.11; H, 2.14.

***anhydro*-4-Hydroxy-2-phenyl-5-(thiobenzoylthiomethylcarbonyl)-1,3-dithiolium Hydroxide (2, R = Ph; R^1 = $COCH_2SCSPh$).** Thiobenzoylthioglycollic acid (4.25 g), dissolved in acetic anhydride (30 ml), was treated with boron trifluoride etherate (2 ml) and the reaction mixture was warmed at ca. 60 °C for 1 h when the yellow precipitate dissolved. The cooled reaction mixture was poured onto ice (100 g) and the product collected, washed with water, and dried. It crystallized from chloroform–ether as red needles: 2.0 g (52%); mp 185–186 °C dec (lit.[9] mp 185–186 °C); ir (KBr) 1690, 1590 cm^{-1} (CO); NMR ($CDCl_3$) δ 3.75–4.01 and 4.08–4.33 (AB d, 2, J = 16.5 Hz, $-CH_2-$), 7.48 (m, 10, aromatic); $M^{\cdot+}$ 388 (5).

Anal. Calcd for $C_{18}H_{12}O_2S_4$: C, 55.67; H, 3.12. Found: C, 55.51; H, 3.19.

Cycloaddition Reactions of *anhydro*-2-Aryl-4-hydroxy-1,3-dithiolium Hydroxides. A. With Acetylenic Dipolarophiles. The mesoionic compound (**2**, R = Ph; R^1 = H) (1.94 g, 0.01 mol) and dimethyl acetylenedicarboxylate (1.42 g, 0.01 mol) in anhydrous benzene (50 ml) were heated under reflux for 3 h. After evaporation of the benzene, the crystalline residue was chromatographed on neutral alumina using chloroform as eluent. Dimethyl 2-phenylthiophene-3,4-dicarboxylate (**5**, R = Ph; R^1 = H; R^2 = $COOCH_3$) crystallized from chloroform–petroleum ether (bp 30–60 °C) as cream needles: 1.1 g (40%); mp 70–71 °C; ir (KBr) 1725 cm^{-1} (CO); λ_{max} (CH_3OH) 230 nm (log ϵ 4.28), 275 (3.91); NMR ($CDCl_3$) δ 3.81 (s, 3, 4-$COOCH_3$), 3.83 (s, 3, 3-$COOCH_3$), 7.43 (m, 5, aromatic), 7.98 (s, 1, H_5); $M^{\cdot+}$ 276 (38).

Anal. Calcd for $C_{14}H_{12}O_4S$: C, 60.87; H, 4.38. Found: C, 60.83; H, 4.52.

Dimethyl 2-*p*-methoxyphenylthiophene-3,4-dicarboxylate (**5**, R = *p*-$CH_3OC_6H_4$; R^1 = H; R^2 = $COOCH_3$) obtained from **2** (R = *p*-$CH_3OC_6H_4$; R^1 = H) as above, separated as cream needles from chloroform–petroleum ether: 47%; mp 100–101 °C; ir (KBr) 1725, 1720 cm^{-1} (CO); λ_{max} (CH_3OH) 240 nm (log ϵ 4.41), 275 (4.83); NMR ($CDCl_3$) δ 3.83 (s, 6, 3- and 4-$COOCH_3$), 3.85 (OCH_3), 6.83–6.98 (AB d, 2, J = 9.0 Hz, aromatic), 7.36–7.51 (AB d, 2, J = 9.0 Hz, aromatic), 7.90 (s, 1, H_5); $M^{\cdot+}$ 306 (70).

Anal. Calcd for $C_{15}H_{14}O_5S$: C, 58.82; H, 4.61. Found: C, 58.70; H, 4.49.

Dimethyl 2-*p*-chlorophenylthiophene-3,4-dicarboxylate (**5**, R = *p*-ClC_6H_4; R^1 = H; R^2 = $COOCH_3$), obtained from **2** (R = *p*-ClC_6H_4; R^1 = H), was chromatographed on Kieselgel g using chloroform as eluent. It crystallized from petroleum ether as pale cream prisms: 44%; mp 80–82 °C; ir (KBr) 1725, 1710 cm^{-1} (CO); λ_{max} (CH_3OH) 233 nm (log ϵ 4.36), 275 (4.03); NMR ($CDCl_3$) δ 3.86 (s, 3, 4-$COOCH_3$), 3.90 (s, 3, 3-$COOCH_3$), 7.42 (s, 4, aromatic), 8.0 (s, 1, H_5); $M^{\cdot+}$ 310 (78).

Anal. Calcd for $C_{14}H_{11}ClO_4S$: C, 54.11; H, 3.57. Found: C, 54.24; H, 3.57.

3,4-Dibenzoyl-2-phenylthiophene (**5**, R = Ph; R^1 = H; R^2 = COPh) prepared from **2** (R = Ph; R^1 = H) and dibenzoylacetylene after chromatography on silica gel ($CHCl_3$) afforded cream prisms from chloroform–petroleum ether (bp 30–60 °C): 68%; mp 160–161 °C; ir (KBr) 1670, 1645 cm^{-1} (CO); λ_{max} (CH_3OH) 255 nm (log ϵ 4.62); NMR ($CDCl_3$) δ 8.2–8.0 (m, 15, aromatic), 7.83 (s, 1, H_5); $M^{\cdot+}$ 368 (95).

Anal. Calcd for $C_{24}H_{16}O_2S$: C, 78.25; H, 4.38. Found: C, 78.44; H, 4.19.

B. Olefinic Dipolarophiles. The mesoionic compound **2** (R = Ph; R^1 = H) (0.5 g) and *N*-phenylmaleimide (0.50 g) in dry benzene (100 ml) were heated under reflux for 6 h. After evaporation of the benzene, the residue was chromatographed on Kieselgel g using chloroform as eluent. The adduct (**8**, R = Ph) crystallized from chloroform–ether as colorless needles: 53%; mp 191–193 °C; ir (KBr) 3080, 3020, 2960, 2950, 1730 cm^{-1} (C=O); λ_{max} (CH_3OH) 200 nm (log ϵ 4.91), 215 sh (4.27); NMR (Me_2SO-d_6) δ 3.93 (dd, 1, J_{AB} = 6.6, J_{BC} = 1.0 Hz, H_5), 4.29 (AB d, 1, J_{AB} = 6.6 Hz, H_6), 4.88 (d, 1, J_{BC} = 1.0 Hz, H_4), 7.58–7.13 (m, 10, aromatic); mass spectrum *m/e* (rel intensity) 307 (42), 160 (100).

Anal. Calcd for $C_{19}H_{13}NO_3S_2$: C, 62.13; H, 3.57; N, 3.81. Found: C, 62.00; H, 3.50; N, 3.70.

The corresponding 2-*p*-methoxyphenyl analogue (**8**, R = *p*-$CH_3OC_6H_4$), obtained from **2** (R = *p*-$CH_3OC_6H_4$; R^1 = H), crystallized from chloroform–ether as colorless needles: 60%; mp 173–176 °C; ir (KBr) 1780, 1710, 1610 cm^{-1} (CO); λ_{max} (CH_3OH) 198 nm (log ϵ 4.66), 223 (4.33); NMR ($CDCl_3$) δ 3.8 (s, 3, OCH_3), 3.9 (dd, 2, J_{AB} = 6.5, J_{BC} = 1.0 Hz, H_5), 4.25 (d, 1, J_{AB} = 6.5 Hz, H_6), 4.85 (d, 1, J_{BC} = 1.0 Hz, H_4), 7.53–6.87 (m, 9, aromatic); mass spectrum *m/e* (rel intensity) 365 (4), 337 (82), 190 (100).

Anal. Calcd for $C_{20}H_{15}NO_4S_2$: C, 60.45; H, 3.81; N, 3.53. Found: C, 60.45; H, 3.81; N, 3.53.

The 2-*p*-chlorophenyl analogue (**8**, R = *p*-ClC_6H_4), prepared from **2** (R = *p*-ClC_6H_4; R^1 = H), crystallized from chloroform–ether as colorless prisms: 58%; mp 205–207 °C; ir (KBr) 1780, 1710, 1600 cm^{-1} (CO); λ_{max} (CH_3OH) 200 nm (log ϵ 4.61), 223 (4.34); NMR (Me_2SO-d_6) δ 5.18 (dd, 1, J_{AB} = 6.5, J_{BC} = 1.0 Hz, H_5), 4.73 (ABd, 1, J_{AB} = 6.5 Hz, H_6), 5.16 (d, 1, J_{BC} = 1.0 Hz, H_4), 7.78–7.08 (m, 9, aromatic); mass spectrum *m/e* (rel intensity) 343 (21), 341 (55), 196 (40), 194 (100).

Anal. Calcd for $C_{19}H_{12}ClNO_3S_2$: C, 56.78; H, 3.01; N, 3.49. Found: C, 56.64; H, 3.04; N, 3.36.

The mesoionic compound **2** (R = Ph; R^1 = H) (1.94 g) and acrylonitrile (100 ml) were refluxed for 3 h, the excess acrylonitrile removed in vacuo, and the residue chromatographed on silica gel ($CHCl_3$). The 1:1 adduct, 6-α-cyano-1-phenyl-2,7-dithiabicyclo[2.2.1]heptan-3-one[26] (**9**, R = CN) crystallized from chloroform–petroleum ether as colorless prisms: 53%; mp 105 °C; ir (KBr) 3010, 2960, 2250 (C≡N), 1710 cm^{-1} (C=O); λ_{max} (CH_3OH) 200 nm (log ϵ 4.33); NMR ($CDCl_3$) δ 7.49 (m, 5, aromatic), 4.54 (dd, 1, H_4), 4.05 (dd, 1, $H_{6\alpha}$), 3.00 (m, 1, $H_{5\alpha}$), 2.76 (m, 1, $H_{5\beta}$), $J_{4,5\alpha}$ = 1.3, $J_{4,5\beta}$ = 4.7, $J_{5\alpha,6\alpha}$ = 7.7, $J_{5\beta,6\alpha}$ = 4.0 Hz; $M^{\cdot+}$ 247 (4).

Anal. Calcd for $C_{12}H_9NOS_2$: C, 58.30; H, 3.67; N, 5.67. Found: C, 58.44; H, 3.62; N, 5.60.

The mesoionic compound **2** (R = Ph; R^1 = H) (1.94 g) and ethyl acrylate (100 ml) were refluxed for 1 h, the excess ethyl acrylate removed in vacuo, and the residue was then chromatographed on silica gel ($CHCl_3$). The 1:1 adduct 6-carboethoxy-1-phenyl-2,7-dithiabicyclo[2.2.1]heptan-3-one (**9**, R = $COOC_2H_5$) crystallized from chloroform–petroleum ether as colorless needles: 57%; mp 84–86 °C; ir (KBr) 3070, 3045, 3100, 2980, 2945, 2920, 2880, 1730 br cm^{-1} (C=O); λ_{max} (CH_3OH) 200 nm (log ϵ 4.60); NMR ($CDCl_3$) δ 7.36 (m, 5, aromatic), 4.43 (dd, 1, H_4), 3.94 (dd, 1, $H_{6\alpha}$), 3.73 (q, 2, J = 7.0 Hz, CH_2), 2.70 (m, 2, H_5), 0.76 (t, 3, J = 7.0 Hz), $J_{H_4,H_{5\alpha}}$ = 1.7, $J_{4,5\beta}$ = 4.0, $J_{5\alpha,5\beta}$ = 7.5, $J_{5\alpha,6\alpha}$ = 7.0, $J_{5\beta,6\alpha}$ = 5.0 Hz; $M^{\cdot+}$ 294 (4).

Anal. Calcd for $C_{14}H_{14}O_3S_2$: C, 57.14; H, 4.76. Found: C, 57.28; H, 4.79.

C. Azirines. 2,3-Diphenylazirine (0.965 g, 5.0 mmol) and **2** (R = R^1 = Ph) (1.35 g, 5.0 mmol) were refluxed in xylene for 72 h. After removal of the solvent the residual dark oil was chromatographed on silica gel using benzene as eluent. Recrystallization of the major fraction from ethanol gave **11** (R = Ph) as colorless prisms: 0.96 g (2.07 mmol) (41%); mp 195 °C; ir (KBr) 1690 cm^{-1}; λ_{max} (CH_3OH) 244 nm (log ϵ 4.40); NMR ($CDCl_3$) δ 8.18–6.76 (m, 20, aromatic), 5.66 (s, 1, H); $M^{\cdot+}$ 463 (4).

Anal. Calcd for $C_{29}H_{21}NOS_2$: C, 75.13; H, 4.57; N, 3.02. Found: C, 74.91; H, 4.61; N, 3.07.

The endo isomer **12** (R = Ph), mixed with the exo isomer above, was finally separated by PLC and purified by recrystallization from ethanol, forming colorless plates: 0.09 g (0.2 mmol), 4%; mp 229 °C; ir (KBr) 1690 cm^{-1} (CO); NMR ($CDCl_3$) δ 8.21–6.73 (m, 20, aromatic), 5.95 (s, 1, H); $M^{\cdot+}$ 463 (3).

3-Methyl-2-phenylazirine (1.31 g, 10 mmol) and **2** (R = R^1 = Ph) (2.70 g, 10 mmol) were refluxed in *p*-xylene (50 ml) for 11 h. Removal of solvent gave a brown oil which was chromatographed over silica gel and eluted with benzene–hexane (4:1) to give a colorless residue, recrystallizing from ethanol as fine, colorless prisms of **11** and **12** (R = CH_3): 2.27 g (5.66 mmol), 57%; mp 123–125 °C; ir (KBr) 1680 cm^{-1} (CO); λ_{max} (CH_3OH) 243 nm (log ϵ 4.09); NMR ($CDCl_3$) δ 8.16–6.96 (m, 15, aromatic), 4.45 and 3.71 (q, 1, J = 6.0 Hz, H), 1.35 and 1.11 (d, 3, J = 6.0 Hz, CH_3); $M^{\cdot+}$ 401 (1).

Anal. Calcd for $C_{24}H_{19}NOS_2$: C, 71.81; H, 4.77; N, 3.49. Found: C, 71.61; H, 4.72; N, 3.44.

Oxidation of 11 (R = Ph) with *m*-Chloroperbenzoic Acid. A solution of the adduct (0.1 g, 0.21 mmol) in dichloromethane (10 ml) was treated with *m*-chloroperbenzoic acid (0.045 g, 0.25 mmol) and the mixture was stirred for 16 h. The precipitate was filtered, and the filtrate was washed with water (2 × 10 ml) and dried over sodium sulfate. The solvent was removed and the residue was recrystallized from chloroform–ethanol to give fine, colorless needles of **13** (R = Ph): 0.054 g (0.11 mmol), 53%; mp 214 °C; ir (KBr) 1690 (CO), 1177 cm^{-1} (SO); NMR ($CDCl_3$) δ 8.16–6.90 (m, 20, aromatic), 5.76 (s, 1, H); $M^{\cdot+}$ 479 (1).

Anal. Calcd for $C_{29}H_{21}NO_2S_2$: C, 72.64; H, 4.42; N, 2.92. Found: C, 72.68; H, 4.48; N, 2.89.

Oxidation of 11–12 (R = CH_3) with *m*-Chloroperbenzoic Acid. The mixture of adducts (1.0 g, 0.25 mmol) was treated in dichloromethane (10 ml) with *m*-chloroperbenzoic acid (0.51 g, 3 mmol) in dichloromethane (5 ml). The mixture was stirred for 20 h and the precipitated solid was filtered. Workup of the filtrate as above gave an oil which crystallized from chloroform–ethanol as colorless plates of **14** (R = CH_3): 0.52 g (0.12 mmol), 50%; mp 193 °C; ir (KBr) 1700 (CO), 1085 cm^{-1} (SO); NMR ($CDCl_3$) δ 8.06–7.13 (m, 15, aromatic), 5.48 (q, 1, J = 6.0 Hz, H), 1.18 (d, 3, J = 6.0 Hz, CH_3); $M^{\cdot+}$ 417 (1).

Anal. Calcd for $C_{24}H_{19}NO_2S_2$: C, 69.05; H, 4.59; N, 3.36. Found: C, 69.23; H, 4.66; N, 3.36.

Registry No.—**2** (R = Ph; R^1 = H), 58426-74-7; **2** (R = *p*-$CH_3OC_6H_4$; R^1 = H), 58426-75-8; **2** (R = *p*-ClC_6H_4; R^1 = H), 58426-76-9; **2** (R = Ph; R^1 = $COCH_2SCSPh$), 58426-77-0; **2** (R = R^1 = Ph), 58426-78-1; **3** (R = Ph; R^1 = H), 942-91-6; **3** (R = *p*-$CH_3OC_6H_4$; R^1 = H), 38204-31-8; **3** (R = *p*-ClC_6H_4; R^1 = H), 38204-36-3; **5** (R = Ph; R^1 = H; R^2 = $COOCH_3$), 23436-87-5; **5** (R = *p*-$CH_3OC_6H_4$; R^1 = H; R^2 = $COOCH_3$), 23436-88-6; **5** (R = *p*-ClC_6H_4; R^1 = H; R^2 = $COOCH_3$), 58426-79-2; **5** (R = Ph; R^1 = H; R^2 = COPh), 58426-80-5; **8** (R = Ph), 58426-81-6; **8** (R = *p*-$CH_3OC_6H_4$), 58426-82-7; **8** (R = *p*-ClC_6H_4), 58426-83-8; **9** (R = CN), 58426-84-9; **9** (R = $COOC_2H_5$), 58426-85-0; **11** (R = Ph), 58426-86-1; **11** (R = CH_3), 58426-87-2; **12** (R = Ph), 58462-43-4; **12** (R = CH_3), 58462-44-5; **13** (R = Ph), 58426-88-3; **14** (R = CH_3), 58426-89-4; dimethyl acetylenedicarboxylate, 762-42-5; dibenzoylacetylene, 1087-09-8; *N*-phenylmaleimide, 941-69-5; acrylonitrile, 107-13-1; ethyl acrylate, 140-88-5; 2,3-diphenylazirine, 16483-98-0; 3-methyl-2-phenylazirine, 16205-14-4.

References and Notes

(1) (a) Support of this work by U.S. Public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged. (b) Presented in part in a preliminary communication: K. T. Potts and U. P. Singh, *Chem. Commun.*, 569 (1969).

(2) For a recent review see N. Lozac'h, *Adv. Heterocycl. Chem.*, **13**, 161 (1971); E. Klingsberg, *Q. Rev., Chem. Soc.*, **23**, 537 (1969).

(3) For a recent review see E. Campaigne, *Q. Rep. Sulfur Chem.*, **5**, 275 (1970).

(4) E.g., see M. Ahmed, J. M. Buchshriber, and D. M. McKinnon, *Can. J. Chem.*, **48**, 1991 (1970), and references cited therein.

(5) For a recent review see M. Ohta and H. Kato in "Non-Benzenoid Aromat-

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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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.