ceric ammonium nitrate (5.5 g) was added and the mixture was left at room temperature overnight. The solvent was evaporated, the residue was extracted with chloroform, and upon evaporation of the solvent the product was crystallized from methanol (yield 0.85 g, 88%): mp 143–145°; nmr ($CDCl_3$) τ 2.19 (d, H_5), 2.86 (d, H_4), 7.00 (s, 6-SOMe), 7.40 (s, 3-SMe), $J_{4,5}$ = 8.5 Hz; ir 1049 (SO), 1332 cm^{-1} (N–O).

Anal. Calcd for $C_6H_8N_2O_2S_2$: N, 13.72; S, 31.34. Found: N, 13.65; S, 31.20.

6-Chloro-3-methylthiopyridazine 1-Oxide (20, R = SMe, R_1 = Cl).—To a stirred solution of 3,6-dichloropyridazine 1-oxide (33 g) in toluene (200 ml) at 70–85° was added dropwise an equivalent amount of potassium methanethiolate in methanol. After 5 hr the solvent was evaporated to dryness. The residue was treated with water and recrystallized from methanol (yield 10 g, 28%): mp 192–193°; mass spectrum M^+ 176; nmr ($CDCl_3$) τ 2.65 (d, H_5), 2.93 (d, H_4), 7.53 (s, SMe), $J_{4,5}$ = 9.0 Hz; ir 1340 cm^{-1} (N–O).

Anal. Calcd for $C_5H_5ClN_2OS$: N, 15.86; S, 18.15. Found: N, 15.74; S, 18.30.

6-Chloro-3-methylsulfinylpyridazine 1-Oxide (20, R = MeSO, R_1 = Cl).—A mixture of the above compound (0.9 g), glacial acetic acid (10 ml), hydrogen peroxide (0.25 g), and a small amount of sodium tungstate was left at room temperature. The separated crystals were crystallized from *n*-hexane and ethyl acetate (1:1) (yield 0.9 g, 92%): mp 131–132°; nmr ($CDCl_3$) τ 1.93 (d, H_5), 2.60 (d, H_4), 6.95 (s, SOMe), $J_{4,5}$ = 9.0 Hz; ir 1359 cm^{-1} (N–O), 1063 cm^{-1} (SO).

Anal. Calcd for $C_5H_5ClN_2O_2S$: N, 14.54; S, 16.64. Found: N, 14.44; S, 16.40.

6-Chloro-3-methylsulfonylpyridazine 1-Oxide (20, R = $MeSO_2$, R_1 = Cl).—The procedure was as described in the above case, except that the amount of hydrogen peroxide was greater (1.0 g) and reaction temperature 50° (1 hr). The product, obtained after evaporation of the solvent, was crystallized from *n*-hexane and ethyl acetate (1:1) (yield 0.6 g, 57%): mp 152°; mass spectrum M^+ 208; nmr ($CDCl_3$) τ 1.67 and 2.68 (d, H_4 and H_5), 6.55 (s, SO_2Me), $J_{4,5}$ = 9.0 Hz.

3-Hydrazino-6-methylsulfonylpyridazine (19, R = $NHNH_2$, R_1 = $MeSO_2$).—A suspension of **9** (1.2 g) in ethanol (7 ml) was treated with hydrazine hydrate (0.5 g of 100%), and the mixture was heated under reflux for 2 hr. Upon cooling on ice, the separated product was filtered and crystallized from ethanol (yield 0.85 g, 84%): mp 178–179°; nmr (DMSO-d_6) τ 2.87 (d, H_4), 2.22 (d, H_5), 6.73 (s, SO_2Me), 1.05 (broad, $NHNH_2$), 5.45 (broad, $NHNH_2$), $J_{4,5}$ = 9.0 Hz.

Anal. Calcd for $C_5H_8N_4O_2S$: N, 29.78; S, 17.01. Found: N, 29.75; S, 17.40.

6-Methylsulfonyl-3-piperidinopyridazine (19, R = $N(CH_2)_5$, R_1 = $MeSO_2$) was prepared in a similar way, except that *N*,*N*-dimethylformamide was used as solvent (at 60°). After addition of water the product separated and was crystallized from *n*-hexane and ethyl acetate (1:1) (yield 1.1 g, 90%): mp 124–125°; nmr ($CDCl_3$) τ 3.00 (d, H_4), 2.20 (d, H_5), 6.65 (s, SO_2Me), 6.20 and 8.25 (m, piperidine part), $J_{4,5}$ = 9.4 Hz.

Anal. Calcd for $C_{10}H_{15}N_3O_2S$: N, 17.42; S, 13.26. Found: N, 17.62; S, 13.26.

3-Hydrazino-6-methylsulfonylpyridazine 1-Oxide (20, R = $NHNH_2$, R_1 = $MeSO_2$).—The procedure was the same as in the case of the deoxygenated analog and 3,6-bis(methylsulfonyl)-pyridazine 1-oxide was used as starting material: mp 190–192° (from water, yield 83%); mass spectrum M^+ 204.

6-Methylsulfonyl-3-piperidinopyridazine 1-Oxide (20, R = $N(CH_2)_5$, R_1 = $MeSO_2$).—The compound was synthesized from 3,6-bis(methylsulfonyl)pyridazine 1-oxide in the same manner as described for the deoxygenated analog: mp 163–165° (from *n*-hexane and ethyl acetate (1:1), 71% yield); nmr (DMSO-d_6) τ 2.20 (d, H_5), 2.53 (d, H_4), 6.65 (s, 6-SO_2Me), 6.40, and 8.35 (m, piperidine part), $J_{4,5}$ = 9.2 Hz; ir 1361 cm^{-1} (N–O).

Anal. Calcd for $C_{10}H_{15}N_3O_3S$: N, 16.33; S, 12.44. Found: N, 16.61; S, 12.60.

Registry No.—**1**, 7145-61-1; **2**, 40953-86-4; **3**, 7145-62-2; **4**, 40953-88-6; **5**, 37813-54-0; **6**, 40953-90-0; **7**, 40953-91-1; **8**, 40953-92-2; **9**, 40953-93-3; **10**, 40953-94-4; **11**, 40953-95-5; **12**, 40953-96-6; **13**, 40953-97-7; **14**, 40953-98-8; **15**, 40953-99-9; **16**, 40954-00-5; **17**, 40953-96-6; **18**, 40954-02-7; **19** (R = SOMe, R_1 = OMe), 40954-03-8; **19** (R = $MeSO_2$, R_1 = OMe), 40954-04-9; **19** (R = $NHNH_2$, R_1 = $MeSO_2$), 40954-05-0; **19** (R = $N(CH_2)_5$, R_1 = $MeSO_2$), 40954-06-1; **20** (R = SMe, R_1 = Cl), 40954-07-2; **20** (R = MeSO, R_1 = Cl), 40954-08-3; **20** (R = $MeSO_2$, R_1 = Cl), 40954-09-4; **20** (R = $NHNH_2$, R_1 = $MeSO_2$), 40954-10-7; **20** [R = $N(CH_2)_5$, R_1 = $MeSO_2$], 40954-11-8; potassium methanethiolate, 26385-24-0; sodium methoxide, 124-41-4; 3,6-dichloropyridazine, 25974-26-9.

Photolysis and Spectral Properties of Some *N*-Sulfonyliminopyridinium Ylides

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The photolyses of the title compounds have been studied at different wavelengths and in different solvent systems. The main products are either the 1-sulfonyl-1,2-diazepine or the sulfonamide, depending on the reaction conditions. In no case was any evidence obtained for the formation of singlet sulfonyl nitrenes, although the sulfonamides may arise from triplet nitrene. The uv, nmr, and mass spectra of some of the compounds studied are reported and discussed briefly.

Sulfonyl nitrenes are almost always generated by the thermolysis of sulfonyl azides at 120° or higher.[1] In view of the observation that *N*-sulfonylazepines are the products of kinetic control of the reaction of singlet sulfonyl nitrenes with aromatic substrates while the *N*-phenylsulfonamides are the products of thermodynamic control,[2] it was desirable to develop a method of generating sulfonyl nitrenes at low (preferably ambient, or below) temperatures.

Of the various possible methods considered, photolysis of sulfonyl azides appeared the most obvious. Unfortunately, photolysis of aliphatic and aromatic sulfonyl azides in nonprotic, nonpolar solvents such as benzene or cyclohexane, or in a polar solvent such as pyridine, produces insoluble high-melting materials that have not been characterized.[3-5] When, however, the photolysis of methanesulfonyl azide was carried out in benzene at 25° such that the walls of the photolysis apparatus were not coated with tar, a very small amount of *N*-mesylazepine was isolated.[4] The only sulfonyl azide known to photolyze smoothly under these conditions is ferrocenylsulfonyl azide.[6] On the other hand, it has been reported that a number of nitrene derivatives can be produced by the photolysis of appro-

(1) R. A. Abramovitch and R. G. Sutherland, *Fortschr. Chem. Forsch.*, **16**, 1 (1970).

(2) R. A. Abramovitch and V. Uma, *Chem. Commun.*, 797 (1968).

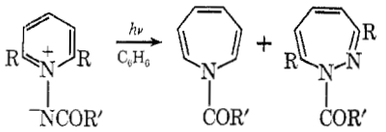
(3) L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963).

(4) V. Uma, Ph.D. Thesis, University of Saskatchewan, 1967.

(5) W. Lwowski and E. Scheiffele, *J. Amer. Chem. Soc.*, **87**, 4359 (1965).

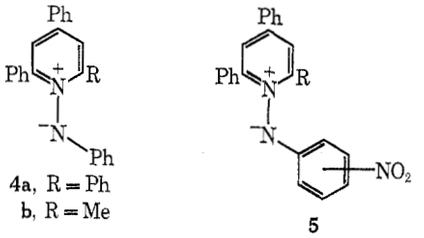
(6) R. A. Abramovitch, C. I. Azogu, and R. G. Sutherland, *Chem. Commun.*, 1439 (1969).

priate pyridinium *N*-ylides. Thus, photolysis of *N*-carbethoxyiminopyridinium ylides (**1**, R′ = OEt) in benzene gives a small amount of *N*-carbethoxyazepine (**2**) (and thence the phenylurethane), in addition to the *N*-carbethoxydiazepine (**3**, R′ = OEt) which is the main



1 **2**, R′ = OEt **3**

product.[7,8] The formation of **2** has been ascribed to the intervention of carbethoxynitrene. Photolysis of *N*-acetyliminopyridinium ylides (**1**, R′ = CH_3) in methylene chloride gave **3** (R′ = CH_3), the corresponding pyridine, and methyl isocyanate. The latter is the product of a photochemical Curtius rearrangement of, presumably, acetylnitrene.[9] Aryl nitrenes have also been postulated as being formed in the photolysis of suitable *N*-aryliminopyridinium ylides. It was concluded[10] that an excited singlet nitrene was formed in the photolysis of *N*,2,4,6-tetraphenyliminopyridinium ylide (**4a**) and of 2-methyl-*N*,4,6-triphenyliminopyridinium ylide (**4b**). On the other hand, photolysis of the



4a, R = Ph
b, R = Me

5

corresponding *N*-nitrophenyliminopyridinium ylides (**5**) gave results which suggested the formation of a nitrene intermediate, but not as an "excited" singlet.[11]

Photolysis of other *N*-imino ylides, in particular 4-imino-1,2,4-triazole derivatives,[12] have also been claimed to give nitrenes. The nature of the products generally indicates that, if a nitrene species is formed in this reaction, it is probably the triplet.

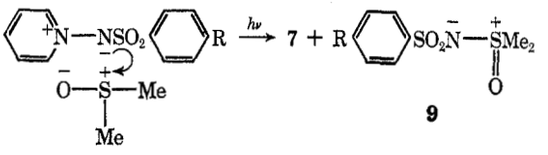
The photolysis of *N*-sulfonyliminopyridinium ylides under various conditions is now examined as a possible ambient-temperature source of singlet sulfonyl nitrenes in solution. The preparation of most of the ylides has already been described.[13] Others are reported in the Experimental Section. After this work was initiated two reports that the photolysis of *N*-sulfonyliminopyridinium ylides (**6**, R = C_6H_5,[14] *p*-$CH_3C_6H_4$[14,15]) gave the *N*-sulfonyldiazepine **7** appeared. Our work confirms this. Since our objective was the generation of sulfonyl nitrenes, we have examined this photolysis under a variety of conditions and find that the products formed vary markedly with the nature of the solvent. The results of photolyses of *N*-benzenesulfonyliminopyridinium ylide (**6**, R = C_6H_5) with 3000 Å radiation in various solvents are summarized in Table I.

TABLE I

PRODUCTS (% YIELD) FORMED IN THE PHOTOLYSIS (3000 Å) OF **6** (R = Ph) IN VARIOUS SOLVENTS

Solvent[a]	**7** (R = Ph)	$C_6H_5SO_2NH_2$ **8**	Recovered **6**	Other
C_6H_6–CH_3CN (10:1 v/v)	76	Trace	21	
C_6H_6–CH_3CN (1:1 v/v)	28	35	40	
Me_2SO	13		10	Sulfoximine **9** (R = Ph) (47%)
$C_6H_5NMe_2$	Trace	65		**10** (5%)
2,6-Lutidine	31	52	23	
C_6H_{12}–CH_2Cl_2 (2:1 v/v)	33	34	9	
Dioxane	28	61	35	**11** (trace)
Me_2CO	4	53		
C_6H_{10}–CH_2Cl_2 (2:1 v/v)	29	55	20	
MeOH	1.7	50	30	

[a] Degassed.



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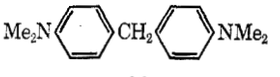
Initial photolyses were carried out in benzene in the expectation that, if singlet sulfonyl nitrenes were formed, they would be trapped either as the *N*-sulfonylazepines (**12**) or the *N*-sulfonylanilines (**13**).[2] Acetonitrile was added to give homogeneous solutions since the ylides are sparingly soluble in benzene and in cyclohexene and insoluble in cyclohexane. No **12** or **13** was ever detected,



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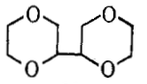

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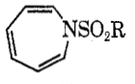

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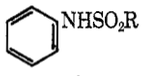

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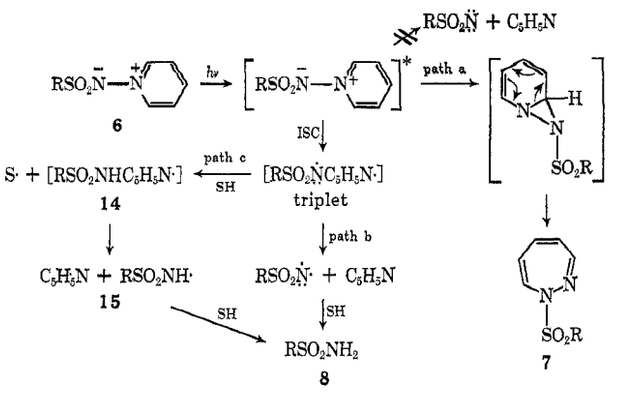
nor was any C–H insertion product[16] observed when the photolysis was carried out in cyclohexane. Neither was any insertion product or the aziridine[17] formed in the photolysis of a cyclohexene solution. When 2,6-lutidine was the solvent, no 3-sulfonylamido derivative[13] of this molecule was observed. Clearly, then, a singlet sulfonyl nitrene is *not* produced in these photolyses.

On the other hand, benzenesulfonamide (**8**, R = C_6H_5) was isolated in almost all the decompositions. This can be viewed as arising *via* path b (Scheme I) through a triplet sulfonyl nitrene which undergoes hydrogen abstraction. Alternatively, one can visualize hydrogen atom abstraction by the photoexcited pyri-

(7) J. Streith, A. Blind, J.-M. Cassal, and C. Sigwalt, *Bull. Soc. Chim. Fr.*, 948 (1969).
(8) T. Sasaki, K. Kanemaksu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35**, 426 (1970).
(9) V. Snieckus, *Chem. Commun.*, 831 (1969).
(10) V. Snieckus and G. Kan, *Chem. Commun.*, 172 (1970).
(11) C. W. Bird, I. Partridge, and D. Y. Wong, *J. Chem. Soc., Perkin Trans. 1*, 1020 (1972).
(12) H. G. O. Becker, *J. Prakt. Chem.*, **312**, 1112 (1971); *Z. Chem.*, **10**, 264 (1970); G. V. Boyd and A. J. H. Summers *J. Chem. Soc. B*, 1648 (1971).
(13) R. A. Abramovitch and T. Takaya, *J. Org. Chem.*, **37**, 2022 (1972).
(14) J. Streith and J.-M. Cassal, *Tetrahedron Lett.*, 4541 (1968).
(15) A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *J. Org. Chem.*, **35**, 433 (1970).
(16) M. F. Sloan, D. S. Breslow, and W. B. Renfrow, *Tetrahedron Lett.*, 2905 (1964).
(17) R. A. Abramovitch, C. I. Azogu, and R. G. Sutherland, *Tetrahedron Lett.*, 1637 (1971).

SCHEME I



dinium ylide taking place to give **14** which would undergo N–N bond cleavage to yield $RSO_2NH\cdot$ (**15**) and pyridine, followed by further hydrogen abstraction by **15** to give the sulfonamide observed (path c, Scheme I). It is not possible at this time to decide between the alternatives. There is some precedent for the formation of excited radical species on photoexcitation; thus irradiation of amines in the presence of aromatic hydrocarbons gives excited charge-transfer complexes (in nonpolar solvents) or radical ions (in aprotic solvents).[18] It has been suggested[8] that the formation of diazepine **3** (R′ = OEt) proceeds *via* an excited triplet state because the yields of **3** obtained were better when **1** (R′ = OEt) was irradiated in acetone (a triplet sensitizer) solution than when it was dissolved in benzene or in dioxane. In contrast to this, photolysis of **6** (R = Ph) in acetone gave only a 4% yield of diazepine **7** (R = Ph) and a 53% yield of hydrogen-abstraction product. Photolysis in benzene, however, gave a high yield of the diazepine and only a trace of the sulfonamide. These results confirm that **8** is a product of a triplet intermediate and suggests that *N*-sulfonyldiazepine arises from a singlet excited state. When dioxane was the solvent, a trace of dioxanyldioxane (**11**) was observed in addition to **7** and **8**, and probably arises by hydrogen abstraction followed by radical coupling. Photolysis of **6** (R = Ph) in *N*,*N*-dimethylaniline (a good electron donor solvent) gave only traces of diazepine: the main product was the sulfonamide, but some 4,4′-methylenebis(*N*,*N*-dimethylaniline) (**10**) was also formed. It is of interest the **10** was also formed in other nitrene reactions: thermolysis of sulfonyl azides[19] and of *p*-nitrophenyl azide[20] in *N*,*N*-dimethylaniline. It was suggested[20] that a formaldehyde precursor, *e.g.*, $PhN(Me)CH_2\cdot$, was the active condensing agent, and this would be in agreement with the present contention that a triplet diradical intermediate is formed in this photolysis.

In view of the above, it seems unlikely that the sulfoximine **9** (R = H) formed from **6** on irradiation in DMSO results from a *free* singlet sulfonyl nitrene being trapped by the solvent. Thermolysis of **6** (R = Ph or *p*-$CH_3C_6H_4$) in DMSO at 100–110° in the presence of copper powder gave only unchanged **6**. Photolysis (2537 Å) of **6** (R = *p*-$CH_3C_6H_4$) in DMSO gave **9** (R = CH_3) (34%) together with **7** (R = *p*-$CH_3C_6H_4$) (12%). We propose that a complex is formed between the singlet excited ylide and this solvent and that **9** is formed concertedly with the elimination of pyridine.

The influence of wavelength on the relative yields of products was examined briefly in the photolysis of **6** (R = *p*-$CH_3C_6H_4$) (λ_{max} 237, 313 mμ) in benzene–acetonitrile (10:1 v/v) solution. The results are given in Table II.

TABLE II

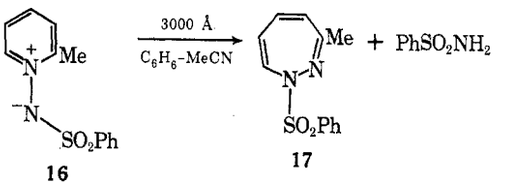
INFLUENCE OF WAVELENGTH ON THE YIELDS OF PRODUCTS FORMED ON PHOTOLYSIS OF **6** (R = *p*-$CH_3C_6H_4$) IN C_6H_6–CH_3CN (10:1 v/v)

Main wavelength, Å[a]	Yield, % 7 (R = *p*-$CH_3C_6H_4$)	*p*-$CH_3C_6H_4SO_2NH_2$ (**8**)	Recovered **6**
2537[b]	14	12	32
3000[c]	74	Trace	24
3500[c]	16	17	47

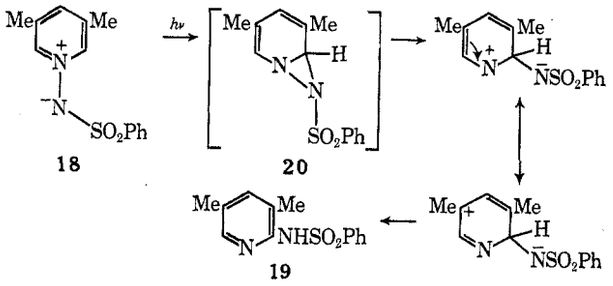
[a] A Rayonet photochemical reactor (RPR-100) was used with RPR-2537 Å (*ca.* 35 W), RPR-3000 Å (*ca.* 21 W), and RPR-3500 Å lamps, respectively. [b] Quartz flask. [c] Pyrex filter.

As can be seen, the best yields of **7** were obtained using 3000 Å lamps but low yields were achieved with the others. On the other hand, high yields of **3** (R′ = OEt) have been reported for the photolysis of **1** (R′ = OEt) in methylene chloride solution at 3500 Å.[15] It is also interesting to note that **7** and **8** are formed in almost equal amounts when 2537 or 3500 Å lamps are used, but only trace amounts of the hydrogen-abstraction product are formed at 3000 Å.

The effect of alkyl groups in the pyridine ring was also briefly studied. Photolysis (3000 Å) of *N*-benzenesulfonylimino-2-methylpyridinium ylide (**16**) in benzene–acetonitrile (10:1 v/v) again gave mainly (54%) 1-benzenesulfonyl-3-methyldiazepine (**17**) to-



gether with a small amount (5%) of benzenesulfonamide. The orientation of the methyl group in **17** was established by its nmr spectrum and is the same as that in the *N*-carbethoxydiazepine obtained from the corresponding 2-picolinium ylide.[15] Thus, cyclization again takes place preferentially to the unsubstituted α position. On the other hand, irradiation of *N*-benzenesulfonylimino-3,5-dimethylpyridinium ylide (**18**) at 3000 Å in C_6H_6–CH_2Cl_2 (10:1 v/v) gave 2-benzenesulfonamido-



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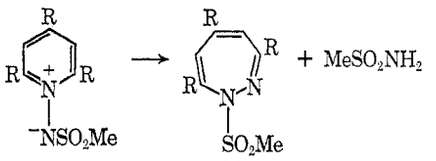
3,5-dimethylpyridine (**19**) (18%) and benzenesulfonamide (33%). 2-Carbethoxyamino-3,5-dimethylpyridine has been obtained similarly from 3,5-dimethyl-1-carbethoxyiminopyridinium ylide.[15] These probably arise by ring opening of the intermediate pyridodiaziridine (**20**), opening to the otherwise unfavorable dipolar species being facilitated by delocalization of the positive charge over the methyl-bearing carbon atoms.

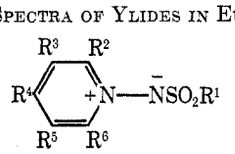
No evidence for the generation of singlet sulfonyl nitrenes could be obtained from the photolysis of *N*-methanesulfonyliminopyridinium ylides (**21**, R = H or CH_3). Again, the only products formed were the diazepines (**22**) and methanesulfonamide. Compound



21 (R = CH_3) was sufficiently soluble in benzene that its irradiation in that solvent alone could be studied. This did not give rise to any new products (other than tars).

Uv, Nmr, and Mass Spectra.—In the course of this work the spectroscopic properties of the ylides and diazepines have been determined. We have already reported[13] the infrared and nmr spectra of the ylides. Table III gives the uv characteristics of ylides studied here and earlier.

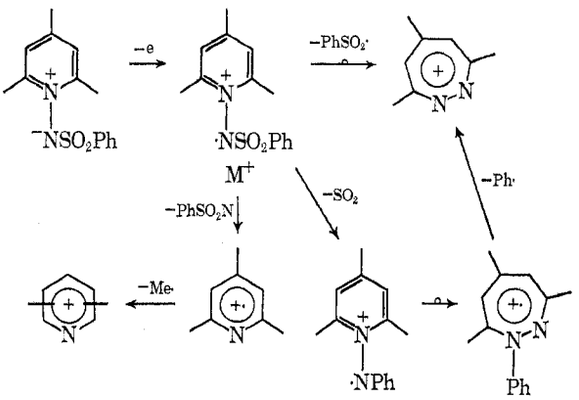
TABLE III
UV SPECTRA OF YLIDES IN EtOH



Compd[a]	Registry no.	λ_{max}, mμ[b]	ε × 10⁻³
R^1 = Ph	28460-28-8	244	11.6
		312	2.0
R^1 = Ph; R^2 = Me	34456-58-1	244	10.7
		311	1.5
R^1 = Ph; R^2 = R^4 = R^6 = Me	34456-63-8	246	12.8
		(295)	1.1
R^1 = Ph; R^4 = CN	34456-64-9	273	8.6
		350	7.7
R^1 = Ph; R^3 = R^5 = Me	34456-61-6	243	13.6
		310	2.4
R^1 = *p*-$CH_3C_6H_4$	40949-56-2	237	13.0
		313	2.1
R^1 = Me	34456-51-4	245	8.3
		308	2.0
R^1 = R^2 = R^4 = R^6 = Me	40949-58-4	245	9.3
		271	4.8
		(295)	0.9
R^1 = *o*-biphenylyl[c]	40949-59-5	238	13.8
		307	3.0
R^1 = *o*-biphenylyl; R^2 = R^4 = R^6 = Me[c]	40949-60-8	241	16.8
		(297)	1.0
R^1 = Ph; R^2,R^3 = R^4,R^5 = —CH=CH—CH=CH—[c]	40949-61-9	255	95.6
		324	1.9
		339	4.2
		356	7.2
		378	4.7

[a] Substituents R^n are H unless otherwise indicated. [b] Figures in parentheses indicate points of inflection. [c] The preparation and properties of these ylides will be reported in a forthcoming paper.

The mass spectra of the ylides all exhibit parent ions, as can be seen from Table IV. When 2 substituents are present, the M^+ peak is of lower intensity than otherwise. These then fragment to give either the diazepinium ion with loss of $PhSO_2$, or N–N bond cleavage occurs to give the pyridinium cations. Since fragments arising from the loss of methyl from the diazepinium ions are of relatively low intensity, it appears as though nuclear methyl groups are lost mainly from the substituted pyridinium radical cation. Loss of SO_2 from the parent ion is also a prominent fragmentation pathway.



A glance at the uv absorption maxima given in Table III clearly suggests that the less intense higher wavelength absorption of the two usually observed for these ylides is associated with a transition of the lone pair of electrons on the imino nitrogen atom. When 2,6 substituents are present in the pyridine ring which would force the RSO_2 group out of coplanarity with that ring, this band moves to higher frequencies, while the lower wavelength band (π,π^*) is relatively unaffected.

The nmr spectral assignments for the diazepines are very similar to those made[15] for the corresponding *N*-carbethoxy derivatives and for the known sulfonyl derivatives.

Experimental Section

Nmr spectra were determined on a Varian HA-100 spectrometer and mass spectra on a CEC 21-104 single focusing instrument at 70 eV.

1-Methanesulfonylimino-2,4,6-trimethylpyridinium Ylide.—A solution of methanesulfonyl hydrazide (5.50 g) and 2,4,6-trimethylpyrilium perchlorate (11.1 g) in methanol (200 ml) was boiled under reflux for 18 hr on a steam bath. The solution was concentrated to 50 ml *in vacuo*, and a solution of KOH (5.5 g) in H_2O (10 ml) was added portionwise with cooling. The mixture was stirred for 1 hr at room temperature, the potassium chlorate which separated was filtered, and the filtrate concentrated and chromatographed on basic alumina. Elution with CH_2Cl_2 gave the desired ylide (8.5 g, 80%): mp 149.5–150.5° (from benzene); mass spectrum *m/e* (rel intensity) 214 (23, M^+), 135 (100, $M^+ - CH_3SO_2\cdot$), 121(19, $M^+ - CH_3SO_2N$).

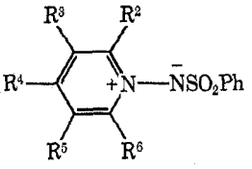
Anal. Calcd for $C_9H_{14}N_2O_2S$: C, 50.45; H, 6.59. Found: C, 50.59; H, 6.55.

Photolysis of 6 (R = Ph) in Benzene–Acetonitrile.—The general procedure used in the photolyses is similar to that illustrated below.

A.—A solution of ylide **6** (R = Ph) (1.17 g) in a mixture of benzene (600 ml) and acetonitrile (60 ml) was irradiated in a Pyrex flask under dry N_2 at room temperature for 24 hr using Rayonet RPR-3000 Å lamps. The yellow solution was evaporated under vacuum to give a brown residue which was chromatographed on a column of silica gel (35 g). Elution with ether–petroleum ether (bp 30–60°) (4:1 v/v) gave 1-benzenesul-

TABLE IV

MASS SPECTRAL DATA FOR *N*-BENZENESULFONYLIMINOPYRIDINIUM YLIDES,[a] *m/e* (RELATIVE INTENSITY)[b,c]



	6	R^3 = Me (34456-58-1)	R^4 = Me (34456-59-2)	R^5 = Me (34456-60-5)	R^3 = R^5 = Me (34456-61-6)	R^2 = R^6 = Me (34456-62-1)	R^2 = R^4 = R^6 = Me (34456-63-8)	R^4 = CN (34456-64-9)
M^+	234 (35)	248 (8)	248 (60)	248 (75)	262 (21)	262 (6)	276 (5)	259 (28)
			247 (21)					
$M^+ - SO_2$	170 (100)	184 (17)	184 (46)	184 (60)	198 (21)	198 (23)	212 (44)	195 (10)
	169 (32)	168 (18)	183 (21)	183 (33)			197 (13)	157 (14)
	157 (15)						196 (18)	
	141 (26)							141 (13)
$M^+ - C_6H_5SO_2\cdot$	93 (16)	107 (100)	107 (54)	107 (56)	121 (30)	121 (100)	135 (100)	118 (26)
			94 (30)					
$M^+ - C_6H_5SO_2N$	79 (15)	93 (26)	93 (83)	93 (100)	107 (100)	107 (22)	121 (28)	104 (67)
					106 (47)	106 (11)	106 (84)	
					94 (25)	94 (19)		
						93 (12)		93 (14)
		92 (14)			92 (21)	92 (67)		
				91 (44)	91 (38)	91 (18)	91 (38)	91 (54)
		79 (39)	80 (30)	80 (53)	79 (45)		79 (35)	
			78 (62)	78 (67)	78 (77)	78 (12)		78 (15)
Ph^+	77 (23)	77 (99)	77 (100)	77 (90)	77 (87)	77 (27)	77 (49)	77 (100)
							67 (15)	76 (13)
		76 (52)	66 (29)	66 (28)	65 (22)	65 (19)	65 (20)	64 (31)
		53 (26)	53 (46)	53 (50)	53 (31)	53 (17)		63 (19)
	52 (11)	52 (19)			52 (24)			
	51 (18)	51 (51)	51 (70)	51 (70)	51 (60)	52 (21)	51 (34)	51 (37)
					50 (24)			50 (28)
	44 (20)				41 (26)	41 (11)	41 (39)	41 (11)
$C_3H_3^+$	39 (12)	39 (30)	39 (40)	39 (60)	39 (52)	39 (21)	39 (34)	39 (22)

[a] Substituent H unless otherwise specified. [b] Only fragment ions with more than 10% relative intensities are reported. [c] Registry numbers found in table headings.

fonyl-(1*H*)-1,2-diazepine (**7**, R = Ph) (76%): mp 147–148°; identical (ir, nmr) with the product described in the literature;[14,15] mass spectrum *m/e* (rel intensity) 234 (11, M^+), 170 (11, $M^+ - SO_2$), 93 (33, $M^+ - PhSO_2\cdot$) (no peak at *m/e* 79 corresponding to the loss of $PhSO_2N$).

Anal. Calcd for $C_{11}H_{10}N_2O_2S$: C, 56.40, H, 4.30. Found: C, 56.31; H, 4.52.

Elution with ether gave diazepine contaminated with traces of benzenesulfonamide (mp 138–144°). The sulfonamide could be resolved from the azepine by thin layer chromatography on silica gel using chloroform–methanol (10:1 v/v) as the developer. Elution with ether–methanol (3:1 v/v) gave unreacted ylide (260 mg, 21%).

B.—When the photolysis was repeated using a 1:1 mixture of benzene and acetonitrile (total volume 660 ml), chromatography as before gave diazepine (28%), benzenesulfonamide (35%), mp 151–153°, undepressed on admixture with an authentic sample, and starting ylide (40%).

Photolysis of 6 (R = Ph) in DMSO.—From **6** (R = Ph) (0.468 g) in DMSO (300 ml) were obtained diazepine **7** (R = Ph) (13%), dimethyl sulfone (53 mg), mp 109–110°, identical with an authentic sample, and *N*-benzenesulfonyldimethylsulfoximine (**9**, R = Ph) (0.219 g, 47%), mp 115–116° (lit.[21] 115°), identical with an authentic sample. Starting material (46 mg) was also recovered.

Photolysis of 6 (R = Ph) in Dioxane.—In addition to the diazepine (28%), mp 146–147°, and benzenesulfonamide (61%), mp 152–154°, there was obtained from **6** (R = Ph) (1.17 g) a crude colorless product (30 mg) which, on tlc, indicated the presence of two components. Fractional crystallization from methanol–ether gave *meso*-dioxanyldioxane (4 mg), mp 156–158° (lit.[22] 157°), mass spectrum *m/e* 174 (M^+). The other component may be the *dl* isomer (lit.[22] mp 131°), but insufficient pure material could be obtained for identification. Starting ylide (35%) was recovered.

Photolysis of 6 (R = Ph) in *N,N*-dimethylaniline gave only benzenesulfonamide (65%), mp 152–154°, and 4,4′-methylenebis(*N,N*-dimethylaniline) (5%), mp 90° (lit.[23] mp 90°).

Photolysis of 1-Methanesulfonyliminopyridinium Ylide (21, R = H).—A suspension of 1-methanesulfonyliminopyridinium ylide (1.03 g) in a mixture of benzene (600 ml) and acetonitrile (100 ml) was irradiated using the RPR-3000 Å lamps for 40 hr. Chromatography of the reaction products on basic alumina gave 1-methanesulfonyl-(1*H*)-1,2-diazepine (**22**, R = H) (75 mg, 7%): mp 110–111° (from ether–light petroleum ether); ir (KBr) (main peaks only) 1625 (w), 1610 (m), 1353 (vs) 1316 (s), 1170 (vs), 961 (m), 787 (m), 765 (s),730 cm^{-1} (s); nmr $\tau_{TMS}^{CDCl_3}$ 7.07 (s, 3 H, $-SO_2CH_3$), 4.28 (dq, $J_{6,7}$ = 7.5 Hz, $J_{5,6}$ = 5.0 Hz, $J_{4,6}$ = 1.0 Hz, 1 H, C_6-H), 4.01 (d, $J_{6,7}$ = 7.5 Hz, 1 H, C_7-H), 3.71 (dd, $J_{4,5}$ = 11.0 Hz, $J_{3,4}$ = 3.5 Hz, $J_{4,6}$ = 1.0 Hz, 1 H, C_4-H), 3.47 (q, $J_{4,5}$ = 11.0 Hz, $J_{5,6}$ = 5.0 Hz, 1 H, C_5-H), 2.72 (d, $J_{3,4}$ = 3.5 Hz, 1 H, C_3-H); mass spectrum *m/e* (rel intensity) 172 (9, M^+), 93 (70, $M^+ - CH_3SO_2\cdot$), 66 (35), 39 (100, $C_3H_3^+$).

Anal. Calcd for $C_6H_8N_2O_2S$: C, 41.85; H, 4.68. Found: C, 42.05, H, 4.68.

Elution with chloroform gave methanesulfonamide (68 mg, 12%), mp 89–91°, identical with an authentic sample. Elution with $CHCl_3$–MeOH gave starting ylide (0.55 g, 55%).

Photolysis of 21 (R = CH_3).—A solution of the ylide (1.07 g) in benzene (600 mg) was irradiated as above for 80 hr. Chromatography of the products yielded the diazepine (**22**, R = Me) (0.35 g, 35%): mp 126.5–127° (from ether–petroleum ether); ir (KBr) (main peaks only) 1642 (s), 1610 (s), 1577 (s), 1378 (s), 1330 (vs), 1200 (s), 1163 (vs), 1065 (s), 990 (s), 970 (s), 845 (s), 780 (s), 735 cm^{-1} (s); nmr $\tau_{TMS}^{CDCl_3}$ 8.11 (s, 3 H, C_5-CH_3)

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7.94 (s, 3 H, C_7-CH_3), 7.80 (s, H, C_3-CH_3), 6.91 (s, 3 H, SO_2-CH_3), 4.28 (br s, 1 H, C_6-H), 3.83 (br s, 1 H), C_4-H); mass spectrum *m/e* (rel intensity) 214 (19, M^+), 135 (100, $M^+ - CH_2SO_2\cdot$), 121 (19, $M^+ - CH_3SO_2N$), 106 (25), 39 (12).

Anal. Calcd for $C_9H_{14}N_2O_2S$: C, 50.45; H, 6.59. Found: C, 50.60; H, 6.59.

Elution with methylene chloride gave methanesulfonamide (60 mg, 12.5%). Elution with chloroform–methanol gave starting ylide (172 mg, 16%).

Photolysis of 1-Benzenesulfonylimino-2-methylpyridinium Ylide (16).—This was carried out in benzene–acetonitrile (6:1 v/v) to give the diazepine **17** (54.1%): mp 118.5–119°; nmr $\tau_{TMS}^{CDCl_3}$ 8.00 (s, 3 H, C_8-CH_3), 4.36 (dq, $J_{6,7}$ = 7.0 Hz, $J_{5,6}$ = $J_{6,7}$ = 3.5 Hz, $J_{4,6}$ = 0.5 Hz, 1 H, C_6-H), 4.04 (dd, $J_{6,7}$ = 7.0 Hz, $J_{5,7}$ = 0.5 Hz, 1 H, C_7-H), 3.58 (d, $J_{5,6}$ = $J_{4,5}$ = 3.5 Hz, 2 H, C_4-H and C_5-H), 2.50 (m, $J_{\alpha,\beta}$ = $J_{\alpha',\beta'}$ = 8 Hz, 3 H, C_β-H, $C_{\beta'}$-H, C_α-H), 2.04 (dd, $J_{\alpha,\beta}$ = $J_{\alpha',\beta'}$ = 8.0 Hz, $J_{\alpha,\gamma}$ = $J_{\alpha',\gamma}$ = 2.0 Hz, 2 H, C_α-H, $C_{\alpha'}$-H); mass spectrum *m/e* (rel intensity) 248 (7, M^+), 107 (100, $M^+ - PhSO_2\cdot$), 93 (21, $M^+ - PhSO_2N$), 77 (70, Ph^+), 39 (37).

Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87. Found: C, 58.33; H, 5.08.

Benzenesulfonamide (5.2%), mp 153–155°, and starting ylide (31%) were also isolated.

Photolysis of 1-Benzenesulfonylimino-3,5-dimethylpyridinium Ylide (18).—This photolysis was effected on a benzene–methylene chloride (10:1 v/v) solution using RPR-3000 Å lamps for 80 hr. Chromatography on basic alumina gave a yellow solid (<1%), mp 118–119°, which could be the diazepine but was not available in sufficient quantity for characterization and 2-benzenesulfonylamino-3,5-dimethylpyridine (**19**) (18%), mp 132° (from benzene–cyclohexane), identical with a sample synthesized from 2-amino-3,5-dimethylpyridine and benzenesulfonyl chloride in pyridine: ir (KBr) (main bands only) 3250 (s), 1600 (vs), 1540 (s), 1408 (s), 1372 (s), 1340 (s), 1245 (s), 1130 (s), 1080 (vs), 983 (s), 936 (s), 740 (s), 720 (s), 695 cm^{-1} (s); mass spectrum *m/e* (rel intensity) 262 (4, M^+), 197 (100, $M^+ - H\cdot - SO_2$), 121 (41, $M^+ - PhSO_2\cdot$), 77 (46), 39 (20).

Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.52; H, 5.38. Found: C, 59.67; H, 5.53.

Benzenesulfonamide (33%) and starting ylide (8.5%), mp 209–211°, were also isolated.

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Registry No.—**7** (R = Ph), 20169-41-9; **17**, 40988-50-9; **19**, 40949-66-4; **22** (R = H), 40949-67-5; **22** (R = Me), 40949-68-6; methanesulfonyl hydrazide, 10393-86-9; 2,4,6-trimethylpyridium perchlorate, 940-93-2.

Reactivity of Thiazole in Electrophilic Reactions as Determined from Solvolysis Rates[1]

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Solvolysis rates for the three isomeric 1-thiazolylethyl chlorides have been determined in 80% ethanol. The general reactivity of thiazole in electrophilic substitution reactions has been discussed and the decreasing order of reactivity of 5-thiazolyl > 4-thiazolyl > phenyl > 2-thiazolyl has been established.

The solvolysis of α-arylethanol derivatives is a useful probe of aromatic reactivity. Streitwieser, *et al.*,[2–4] have recently compared the reactivities of a large number of aromatic hydrocarbons, and the solvolysis rates of the corresponding arylmethyl tosylates. There is good correspondence in the two series, covering a wide variety of types and conditions,[2] and to various semiempirical MO methods;[4] the results lead to a useful set of σ constants for the aromatic moiety, designated σ^+ by Streitwieser.[3]

This concept has been extended to heterocyclic systems by Hill,[5] by the senior author,[6] by Taylor,[7] and by Marino.[8] Particularly pertinent are the observed relationships of reactivity of thiophene and its derivatives[6,9] and of furan and its derivatives.[10]

The solvolysis reaction has several distinct advantages for the investigation of basic heterocyclic systems, as it avoids the uncertainties of whether reaction is occurring *via* the protonated form or the free base. Studies from these laboratories have established σ^+ values for pyridine moieties in this fashion.[11]

In the present study we examine the thiazole system. Each of the isomeric 1-(thiazolyl)ethyl chlorides was prepared and solvolyzed. The data are given in Table I, and the rates are compared to the solvolysis rate for 1-phenylethyl chloride, which is of similar reactivity. (See Table I.)

From the rate data in Table I, we calculate σ^+ values appropriate for the various thiazole moieties,[12] using ρ for the solvolysis −5.12.[13] Thus the replacement $\sigma_{Ar}{}^+$ are as follows: 5-thiazolyl −0.18; 4-thiazolyl −0.01; 2-thiazolyl +0.26.

There have been a number of MO calculations carried out on thiazole. Metzger and his coworkers[14] have recently summarized calculations carried out to various levels of sophistication. All of these methods agree that the reactivity order is 5 > 4 > 2.

The greater reactivity of 1-(5-thiazolyl)ethyl chlo-

(1) Supported in part by a grant from the National Science Foundation, GP-6133X.

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