The Reaction of Sulfonyl Azides with Pyridines and Fused Pyridine Derivatives

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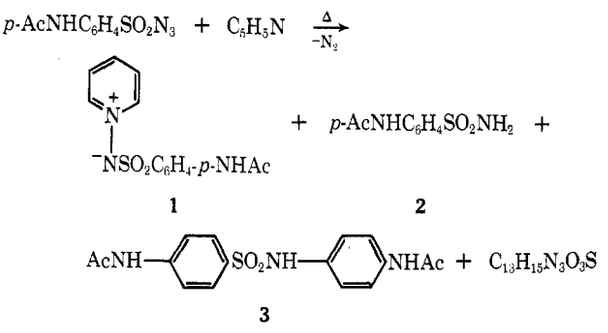
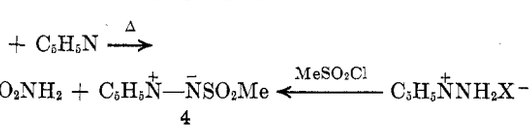
The thermal reaction of sulfonyl azides with pyridines, quinoline, isoquinoline, and acridine has been reexamined and the course of the reaction established unambiguously. In many cases, sulfonylaminopyridines are formed and in most *N*-sulfonyliminopyridinium ylides are obtained. The orientation of the former has been determined and implicates the intervention of a sulfonyl nitrene intermediate. Quinaldine, 1-methylisoquinoline, and 6-methylphenanthridine behave differently and give 1,2,3-triazolo[1,5-*a*]quinoline, 1,2,3-triazolo[5,1-*a*]isoquinoline, and 1,2,3-triazolo[1,5-*f*]phenanthridine, respectively, in high yields. Possible mechanisms for these reactions are discussed as are the spectral properties of the products.

The reaction of sulfonyl azides with pyridine was first studied by Curtius and coworkers,[2] who reported the isolation of compounds they formulated as 2-, 3-, or 4-aminopyridine derivatives. They also obtained the hydrogen abstraction product, the unsubstituted sulfonamide. For example, hydrolysis of the product from 2-naphthylsulfonyl azide and pyridine with hydrochloric acid was said to give 2-aminopyridine (identified as its chloroplatinate) and 2-naphthalenesulfonic acid. Other products were not so characterized. From the reaction of *p*-acetamidobenzenesulfonyl azide with pyridine an aminopyridine derivative was obtained which, by analogy with Curtius' work, was assumed to be the 3 isomer.[3] This reaction was reinvestigated by Buchanan and coworkers,[4a] and by Datta,[4b] who proved, both by degradation and by unambiguous synthesis, that the product was actually *N*-(*p*-acetamidobenzenesulfonimido)pyridinium ylide (**1**). The hydrogen-abstraction product **2** was also obtained, as well as a product of ipso substitution (**3**) by the sulfonyl nitrene, and a compound $C_{13}H_{15}N_3O_3S$ of unknown structure.[4a] The latter needs reinvestigation, since the molecular formula corresponds to a dihydro derivative of **1** or of a *C*-aminopyridine derivative. By implication, it has since been assumed that no aminopyridines were actually formed in the reactions studied by Curtius.[5] Attempts to obtain the corresponding 1-aminoquinolinium derivatives led only to tar formation and the isolation of the hydrogen-abstraction product.[2,6]

In view of the above apparent contradictions, and of our need for 1-iminopyridinium *N*-sulfonyl ylides as potential non azide precursors for the generation of sulfonyl nitrenes, we have reinvestigated the reaction of pyridine and some substituted pyridines with a number of sulfonyl azides, and have extended these studies to quinoline, isoquinoline, acridine, and phenanthridine derivatives.

Thermolysis of methane-, benzene-, or *p*-toluenesulfonyl azide in pyridine itself gave only two identifiable products, the 1-sulfonylimidopyridinium ylide and the unsubstituted sulfonamide. In no case could any product of substitution at carbon be detected, even by tlc or glc. The benzene- and *p*-toluenesulfonylimino ylides are known compounds but the 1-mesyliminopyridinium ylide (**4**) was not and its structure was confirmed by its nmr spectrum and its synthesis from 1-aminopyridinium iodide or sulfate.





On the other hand, thermal decomposition of benzenesulfonyl azide in 2- and 4-picoline, in 2,6-lutidine, and in 2,4,6-collidine gave both the C_3- (**5**) and the N-amination products (**6**), in addition to benzenesulfonamide. No 6-benzenesulfonamido-2-methylpyridine could be detected in the reaction with 2-picoline. No C-amination products were formed, however, in the thermolyses in 3-picoline, 3,5-ludidine, and 4-cyanopyridine, only the ylide **6** and benzenesulfonamide being obtained. The results are summarized in Table I.

The structures of the sulfonamides **5** and the *N*-ylides **6** were determined by spectral and analytical measurements, as well as by the synthesis of authentic samples in some cases.

Infrared Spectra.—The sulfonamides **5** exhibited the two strong SO_2 bands in the normal range[7] of 1320–1340 and 1160–1170 cm^{-1}. The NH stretching band did not appear in its usual position but, instead, a very broad absorption in the 2880–2650 cm^{-1} region was evident (KBr disks of the compounds), suggesting that the sulfonamides existed predominantly in the zwitterionic form **5'** in the solid state. In contrast to the sulfonamides **5**, the *N*-sulfonylimino ylides **6** exhibited two strong bands due to SO_2 in the 1270–1285 and 1130–1140 cm^{-1} regions. This bathochromic shift may be

(1) Postdoctoral Fellow, 1969–1970, on leave from Osaka Prefecture University.

(2) T. Curtius, *J. Prakt. Chem.*, **125**, 303 (1930); T. Curtius and J. Rissom, *ibid.*, **125**, 311 (1930); T. Curtius and G. Kraemer, *ibid.*, **125**, 323 (1930); T. Curtius and K. Vorbach, *ibid.*, **125**, 340 (1930); T. Curtius and H. Derlon, *ibid.*, **125**, 420 (1930).

(3) B. S. Alamela and K. Ganapathi, *Curr. Sci.*, **12**, 119 (1943); *Chem. Abstr.*, **38**, 5492 (1944).

(4) (a) J. N. Ashley, G. L. Buchanan, and A. P. T. Eason, *J. Chem. Soc.*, 60 (1947); G. L. Buchanan and R. M. Levine, *ibid.*, 2248 (1950); (b) P. K. Datta, *J. Indian Chem. Soc.*, **24**, 109 (1947).

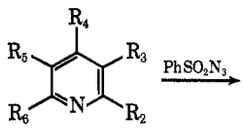
(5) D. S. Breslow in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, p 245.

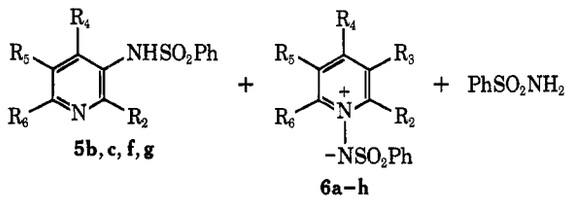
(6) R. J. W. Cremlyn, *J. Chem. Soc.*, 1132 (1965).

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958.

TABLE I

PRODUCTS (%) OBTAINED FROM THERMOLYSIS OF BENZENESULFONYL AZIDE IN PYRIDINES[a]





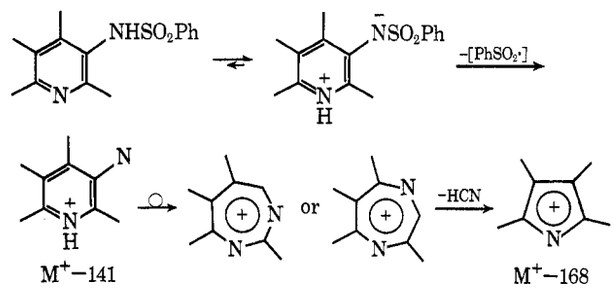
5b, c, f, g 6a–h

	5	6	$PhSO_2NH_2$	Overall yield, %
a		30	>18	>48
b, R_2 = Me; R_6 = H	8.8[b]	37	45	91
c, R_4 = Me	5	18	62	85
d, R_3 = Me		49	23	72
e, R_3 = R_5 = Me		54	37	91
f, R_2 = R_6 = Me	13	18	57	88
g, R_2 = R_4 = R_6 = Me	15	15	61	91
h, R_4 = CN		17	>30	>47

[a] All R_n = H unless specified. [b] Mixture of 3- and 5-benzenesulfonamido-2-methylpyridine.

and orientation in the case of **5**. The chemical shifts and coupling constants are summarized in Tables II and III. From the ratio of the intensities of the two methyl peaks observed in the nmr spectrum of the unresolved mixture of **5b** the molar ratio of 3-benzenesulfonamido-2-methyl- and 5-benzenesulfonamido-2-methylpyridine was determined to be 0.41.

In the mass spectra of the sulfonamides the main fragment ions in addition to M^+ are $M^+ - 141$ ($-C_6H_5SO_2$), $M^+ - 168$ ($-C_6H_5SO_2 - HCN$), and $C_6H_5^+$.

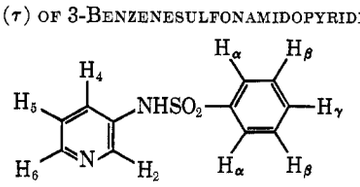


The mass spectral fragmentations of the ylides will be discussed in a future paper.

Authentic samples of the sulfonamides **5** were prepared from the 3-aminopyridine and benzenesulfonyl chloride in pyridine. Some of the ylides **6** were synthesized by the reaction of the appropriate 1-aminopyridinium salt with benzenesulfonyl chloride in the presence of a base. **6f** could not be prepared in this way, though the desired amine was obtained readily. **6g** was more conveniently prepared by the reaction of the 2,4,6-trimethylpyrylium salt **7** with benzenesulfonylhydrazide and a base. The corresponding 2,4,6-triphenylpyrylium salt did not react with benzenesulfonylhydrazide and was recovered unchanged.

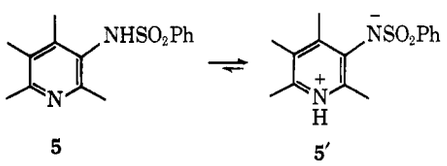
TABLE II

NMR SPECTRA (τ) OF 3-BENZENESULFONAMIDOPYRIDINES IN $CDCl_3$



Compd	H_2	H_4	H_5	H_6	H_α	H_β	H_γ
5b[a] (2,5-)	1.90 d ($J_{2,4}$ 1.5 Hz)	2.50 m	2.95 d ($J_{4,5}$ = 8 Hz)	7.63 (3 H, s, CH_3)	2.42 m		2.50–2.65 m
5b[a] (2,3-)	7.83 (3 H, s, CH_3)	2.50 m	3.00 q ($J_{4,5}$ = $J_{5,6}$ = 8 Hz)	1.80 dd ($J_{5,6}$ = 8; $J_{4,6}$ = 1.5 Hz)	2.42 m		2.50–2.65 m
5c[b]	1.50 s	7.57 (3 H, s, CH_3)	2.37 d ($J_{5,6}$ = 5 Hz)	1.32 d ($J_{5,6}$ = 5 Hz)		1.93 (5H, s)	
5f	7.83 (3 H, s, CH_3)	2.44 d ($J_{4,5}$ = 8 Hz)	3.07 d ($J_{4,5}$ = 8 Hz)	7.54 (3 H, s, CH_3)	2.26 (2 H, dd) ($J_{\alpha\beta}$ = 8 Hz; $J_{\alpha\gamma}$ = 2 Hz)		2.50 (3 H, m)
5g	8.00 (3 H, s, CH_3)	8.18 (3 H, s, CH_3)	3.13 s	7.54 (3 H, s, CH_3)	1.96 (2 H, dd) ($J_{\alpha\beta}$ = 8 Hz; $J_{\alpha\gamma}$ = 2 Hz)		2.44 (3 H, m)

[a] Unresolved mixture of 2,3 and 2,5 isomers. [b] DMSO-d_6 used as solvent in this case.



5 **5′**

due to the delocalization of the electron pair on the imino nitrogen onto the sulfonyl group, rather than partially towards the pyridine ring (as in **5** or **5′**), so that back-donation may not be important in these ylides.

Nmr and Mass Spectra.—The nmr spectra of **5** and **6** permit clear-cut assignments of the structures

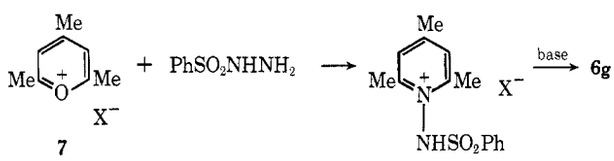


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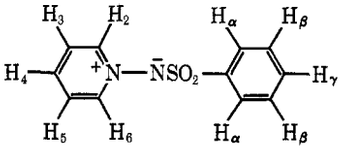
TABLE III

NMR SPECTRA (τ) OF *N*-BENZENESULFONYLIMINOPYRIDINIUM YLIDES IN $CDCl_3$[a]



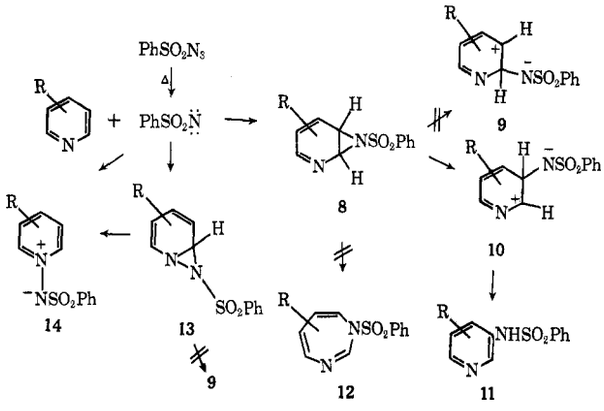
Compd	H_2	H_3	H_4	H_5	H_6	$H\alpha$	$H\beta$	$H\gamma$
6b	7.58 (3 H, s, CH_3)	2.28–2.69 m	2.08 t ($J_{3,4}$ = 8 Hz)	2.28–2.69 m	1.41 d ($J_{5,6}$ = 8 Hz)		2.28–2.69 m	
6c	1.70 d ($J_{2,3}$ = 8 Hz)	2.43–2.67 m	7.46 (3 H, s, CH_3)	2.43–2.67 m	1.70 d	2.27 (2 H, d) ($J_{\alpha\beta}$ = 8 Hz)		2.43–2.67 m
6d	1.70 s	7.60 (3 H, s, CH_3)	2.07–2.35 m	2.41–2.70 m	1.74 d ($J_{5,6}$ = 8 Hz)	2.07–2.35 m		2.41–2.70
6e	1.95 s	7.69 (3 H, s, CH_3)	2.45 s	7.69 (3 H, s, CH_3)	1.95 s	2.30 (2 H, dd), ($J_{\alpha\beta}$ = 8 Hz; $J_{\alpha\gamma}$ = 2 Hz)		2.63 (3 H, m)
6f	7.44 (3 H, s, CH_3)	2.58–2.71 m	2.22–2.39 t	2.58–2.71 m	7.49 (3 H, s, CH_3)	2.29–2.39 m		2.58–2.71 m
6g	7.55 (3 H, s, CH_3)	2.81 s	7.63 (3 H, s, CH_3)	2.81 s	7.55 (3 H, s, CH_3)	2.24 (2 H, dd), ($J_{\alpha\beta}$ = 8 Hz, $J_{\alpha\gamma}$ = 2 Hz)		2.62 (3 H, m)

[a] Where a range of τ is indicated this means that overlapping peaks due to more than one type of proton could not be resolved.

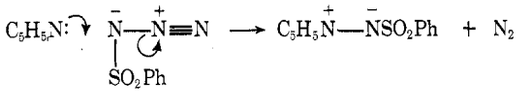
The methanesulfonyl derivative corresponding to **6g** was also most readily prepared in this way from **7** and $MeSO_2NHNH_2$. In contrast to a recent report,[8] we experienced no difficulty in preparing 1-*N*-mesyliminopyridinium ylide, albeit in poor yields, either from the *N*-aminopyridinium salt or from methanesulfonyl azide and pyridine (in the latter case, together with a 70% yield of $MeSO_2NH_2$).

The formation of a 3-sulfonamidopyridine in a number of cases is clearly indicative of the intermediacy of a singlet sulfonyl nitrene in these reactions. Indeed, the exclusive substitution of the 3 position would eliminate a triplet electrophilic nitrene from consideration, since the latter, behaving as an electrophilic radical, might be expected to attack not only the 3, but the 2 and 4 positions as well,[9] but be consistent with the expected behavior of a singlet electrophilic species. The rate-determining step following the elimination of nitrogen would be the addition of the singlet sulfonyl nitrene to the pyridine ring to give a pyridoaziridine intermediate (**8**),[10] which in a fast, product-determining step would undergo ring opening under thermodynamic control conditions[11] to give the observed substitution products.

Ring opening of **8** and **9** would yield a dipolar intermediate in which the developing positive charge would be delocalized over the highly electronegative pyridine ring nitrogen atom, while **8** → **10** would not. The latter route is therefore favored and leads to **11** following a prototropic shift. A similar argument would account for the formation of **11** but no 4-sulfonamidopyridine from a nitrene adduct to the pyridine "3,4



double bond." Formation of the ylide **14** could be accounted for in a similar manner by the selective ring opening of **13**, but more likely (since no **9** is formed; *cf.* ref 11a) by a direct trapping of the electrophilic nitrene intermediate, or by a concerted attack of the pyridine nitrogen lone pair on the azide function with elimination of nitrogen.



It should be possible to distinguish between these possibilities by studying the kinetics of the formation of the ylides. If a nitrene intermediate is a precursor, then the rate of ylide formation should be independent of the pyridine concentration, while a bimolecular process is involved in the concerted process. Such studies are under way now.

No 1,3-diazepine (**12**), the expected product of kinetic control,[11] was observed under our conditions, nor was it possible to trap it, say with TCNE as was used with the *N*-sulfonylazepines,[11] since this trapping agent forms relatively stable charge-transfer complexes with pyridines. Similarly, none of the product of photoisom-

(8) J. Epsztajn, E. Lunt, and A. R. Katritzky, *Tetrahedron*, **26**, 1665 (1970).

(9) R. A. Abramovitch and J. G. Saha, *J. Chem. Soc.*, 2175 (1964); R. A. Abramovitch and M. Saha, *J. Chem. Soc. B*, 733 (1966); R. A. Abramovitch, G. N. Knaus, and V. Uma, *J. Amer. Chem. Soc.*, **91**, 7532 (1969); R. A. Abramovitch, *Intra-Sci. Chem. Rep.*, **3**, 211 (1969).

(10) R. A. Abramovitch, J. Roy, and V. Uma, *Can. J. Chem.*, **43**, 3407 (1965); R. A. Abramovitch and R. G. Sutherland, *Fortsch. Chem. Forsch.*, **16**, 1 (1970).

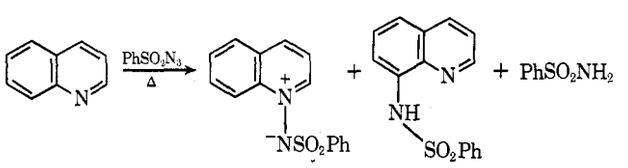
(11) (a) R. A. Abramovitch and V. Uma, *Chem. Commun.*, 797 (1968); (b) J. A. Moore, E. J. Volker, and C. M. Kopay, *J. Org. Chem.*, **36**, 2676 (1971).

erization of **13**, the *N*-sulfonyl-1,2-diazepine,[12] was observed under our thermolysis conditions.

As expected on the basis of an attack of the pyridine nucleus by an electrophilic singlet nitrene, the yield of **5** increased slightly with the presence of electron-donating substituents in the pyridine nucleus and dropped to zero when a 4-cyano group was present. While our mechanism will account readily for the fact that no C-substitution product was observed with 3,5-lutidine, we have no explanation for the lack of formation of **5e** from 3-picoline which still has a vacant β position, unless it is that the methyl group is not in a position where it can delocalize the developing positive charge and hence that the pyridine ring is not nucleophilic enough to undergo addition by the electrophilic sulfonyl nitrene (pyridine itself does not undergo C substitution; see Table I). Alkyl groups at the α and γ positions can delocalize the positive charge (say in **10**) and hence lead to substitution products. If this is so, it might suggest that the transition state for the substitutions resembles an unsymmetrical species whose structure is intermediate between **8** and **10**, *i.e.*, one in which one C–N bond is more developed than the other. That the yields of **6f** and **6g** were not higher than they were may be attributed to steric hindrance by the 2,6-dimethyl group to the attack on the lone pair on nitrogen.

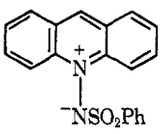
It was shown[10] that the hydrogen abstraction product from the reaction of methanesulfonylnitrene and an aromatic nucleus does not arise by the abstraction of one hydrogen atom at a time (which would lead to the simultaneous production of aryl radicals, for the intermediacy of which no evidence was found) but that two hydrogens were abstracted simultaneously, or almost simultaneously. No bipyridyls were detected in the present study (a small amount of a dipyridylethylene was observed in one case), so that the mechanism of formation of RSO_2NH_2 is not clear.

The reaction was next extended to the fused pyridine derivatives, quinoline, isoquinoline, and acridine. Isoquinoline gave only the hydrogen-abstraction product together with much tar. No ylide could be isolated. Quinoline also gave the hydrogen-abstraction product together with the ylide **15** (12%) and 8-benzenesulfonamidoquinoline (**16**, 1%). No other substitution product was detected, but small amounts of diphenyl disulfide were also obtained. Authentic samples of **15** and **16** were prepared from the 1- and 8-



15 16

aminoquinoline derivatives, respectively. It thus appears that the benzene ring is more susceptible to C attack by the electrophilic nitrene than is the pyridine ring, which is not unexpected. Nitration of quinoline gives the 5- and 8-nitro derivatives, with the former predominating slightly.[13] Acridine gave a low yield (2%) of *N*-benzensulfonyliminoacridinium ylide (**17**) together with some benzenesulfonamide. Again, the low yield of **17** may be attributed to steric hindrance to the approach of the ring nitrogen.



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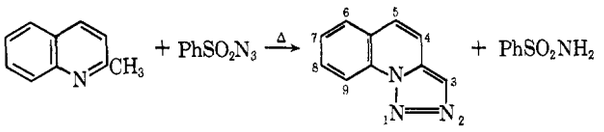
The reaction with α-methylated fused pyridine derivatives gave an unexpected but interesting result. Thus, when quinaldine was heated with benzenesulfonyl azide, benzenesulfonamide was formed, but none of the expected ylide. Instead, a good yield of 1,2,3-triazolo-[1,5-*a*]quinoline (**18**) was obtained. The triazole, which undoubtedly arises from the ring–chain tautomerism of 2-diazomethylquinoline, has previously been obtained less conveniently by the silver oxide oxidation of quinoline-2-aldehyde hydrazone.[14] The triazole ring CH appeared as a singlet at τ 1.96.



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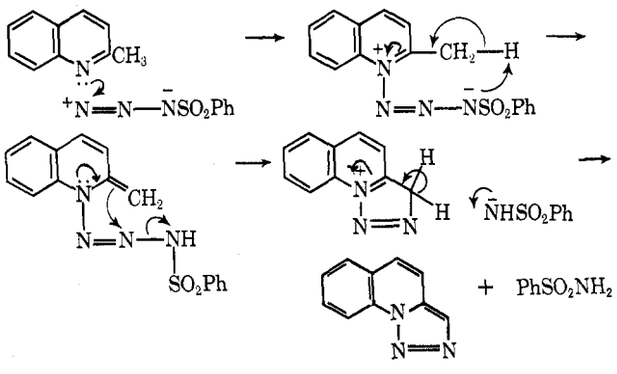
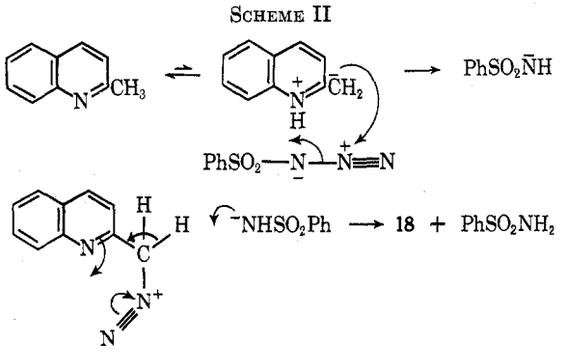
One can write two plausible routes leading from quinaldine to **18**, and these sketched in Schemes I and II. Other routes are conceivable as well.

SCHEME I



SCHEME II

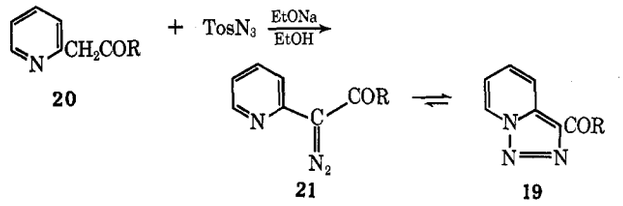


The mechanism outlined in Scheme II is somewhat similar to that proposed for the formation of the keto-triazole **19** by the reaction of an alkyl or aryl (2-pyridyl)-methyl ketone (**20**) with *p*-toluenesulfonyl azide in the

(12) J. S. Streith and J. M. Cassal, *Tetrahedron Lett.*, 4541 (1968); R. A. Abramovitch and T. Takaya, unpublished results.

(13) L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, **62**, 1640 (1940); M. J. S. Dewar and P. M. Maitlis, *J. Chem. Soc.*, 2521 (1957).

(14) J. H. Boyer, R. Borgers, and L. T. Wolford, *J. Amer. Chem. Soc.*, **79**, 678 (1957).

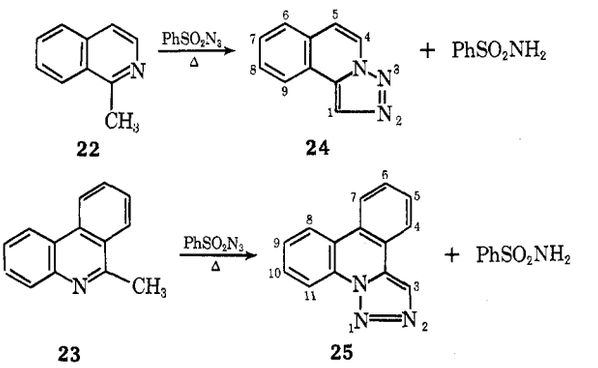


20 **21** **19**

presence of a strong base *via* the diazo ketone intermediate **21**.[15]

It should be pointed out that no such product was observed here in the reactions of the alkylated pyridines themselves with the sulfonyl azides, and that no added base was necessary in the reaction with quinaldine. This confirms that the α-methyl group is much more reactive when attached to a quinoline than to a pyridine nucleus.

The generality of this new reaction was tested by carrying out the decomposition of benzenesulfonyl azide in 1-methylisoquinoline (**22**) and 6-methylphenanthridine (**23**). In both cases the desired 1,2,3-triazolo derivatives were obtained in good yields, together with benzenesulfonamide.



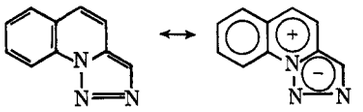
22 **24** **23** **25**

The triazoloisoquinoline **24** exhibited a singlet at τ 1.70 attributed to the triazole ring proton, a 1 H doublet at τ 1.64 ($J_{4,5}$ = 8 Hz) assigned to C_4 H (see numbering above) of the isoquinoline ring, a 1 H doublet at τ 2.98 ($J_{4,5}$ = 8 Hz) assigned to C_5 H, and a 1 H doublet at τ 2.07 ($J_{8,9}$ = 6 Hz) attributed to C_9 H of the isoquinoline ring. **25** exhibited at singlet at τ 2.50 due to the triazole ring proton and a 1 H doublet at τ 0.92 (J = 5 Hz) assigned to C_{11} H of the phenanthridine ring.

The mass spectra of **18**, **24**, and **25** all exhibited strong parent ions, as well as ($M^+ - N_2$) and ($M^+ - N_2 - H$) fragment ions. In the cases of **18** and **24** the ($M^+ - N_2$) ions were the base peaks while the ($M^+ - N_2 - H$) ion was the base peak in **25**.

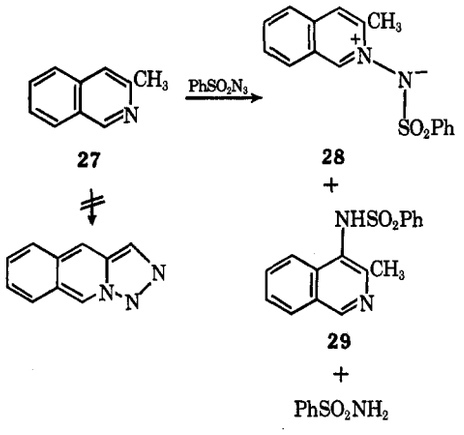
1,2,3-Triazolo[1,5-*a*]quinoline (**18**) proved to be remarkably stable, as was also **25**. The stability of **24** was not investigated. Thus, **18** and **25** were recovered following irradiation in a variety of solvents with light of wavelengths of 2537, 3000, or 3500 Å with or without triplet sensitizers. Attempted thermal decomposition of **18** in solution at temperatures up to 180° with or without a copper catalyst also failed. We are continuing to probe the possible decomposition of these triazoles, whose stability is undoubtedly due to aromatic delocalization as shown in **26** below.

(15) M. Regitz and A. Liedhegener, *Chem. Ber.*, **99**, 2918 (1966); M. Regitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 733 (1967).



26

It is suggested that this aromatic stabilization is an important driving force in the success of this diazo-transfer reaction. On this basis, and also of the fact that the α-methyl group in 3-methylisoquinoline (**27**) would not be expected to be so reactive as that in **22**, we anticipated that such a diazo-transfer reaction would not occur with **27**.[16] Indeed, this has been found to be the case. When **27** was heated with benzenesulfonyl azide, the ylide **28** and benzenesulfonamide were formed, together with a C-substituted sulfonamido derivative. The structure of **28** was unambiguously assigned on the basis of its spectral properties (see Experimental Section). The substitution product has been tentatively identified, mainly on the basis of its nmr spectrum, as being 4-benzenesulfonamido-3-methylisoquinoline (**29**). An authentic sample



27 **28** **29**

of 5-benzenesulfonamido-3-methylisoquinoline had quite different physical properties (but was too unsoluble to permit a determination of its nmr spectrum). **29** exhibited peaks corresponding to C_1 H (s, τ 0.56), C_3 CH_3 (3 H, s, τ 7.45), and C_8 H [d, τ 1.65 (J = 7 Hz) with each branch showing much fine structure]. 3-Methylisoquinoline and 5-amino-3-methylisoquinoline both exhibited a 1 H singlet (in addition to the singlet at lower field due to C_1 H) at τ 2.43 and 2.78, respectively, which is due to C_4 H, as well as multiplets due to C_8 H. No signal corresponding to C_4 H was observed in the spectrum of **29**. If this structural assignment is correct it would indicate that a methyl group in the pyridine ring that can assist the delocalization of the developing charge in the transition state for substitution may stabilize this transition state sufficiently to cause attack of the pyridine ring to be favored over addition to the benzene ring, as was observed in the case of quinoline. In this connection, it would be of interest to study the reaction with 4-methylquinoline to see whether attack takes place in the benzene or pyridine ring and also to see whether or not a diazomethyl compound can be prepared under these conditions when it cannot undergo stabilization by tau-

(16) For such a reaction to occur would require a disruption of the aromatic character of the benzene ring in **27**, allowing other processes to compete effectively with the diazo transfer process.

tomerization to the aromatic species, as can the 2-diazomethyl derivative.

Experimental Section

Melting points are uncorrected. Infrared spectra were determined using a Perkin-Elmer 337 spectrophotometer using KBr disks of the compounds, while nmr spectra were obtained on a Varian HA-100 spectrometer, using deuteriochloroform solutions of the compounds (unless otherwise stated) and TMS as the internal standard.

Reagents.—2-, 3-, and 4-picoline, 2,6- and 3,5-lutidine, and 2,4,6-trimethylpyridine (Reilly Tar and Chemical Corp.) were dried over potassium hydroxide and distilled, as were quinoline and isoquinoline. 1-Methylisoquinoline was prepared by the action of methyllithium on isoquinoline, followed by dehydrogenation of the dihydro derivative at 190° with palladium on charcoal suspended in Freon E-3. It had bp 78–80° (0.8 mm); mass spectrum *m/e* (rel intensity) 143 (100, M^+); picrate mp 216° (lit.[17] mp 225–226°). 6-Methylphenanthridine was prepared by an extension of the method of Taylor and Kalenda.[18] 3-Amino-2,6-lutidine and 3-amino-2,4,6-collidine were prepared by reduction of the corresponding nitro compounds.[19]

Thermal Decomposition of Benzenesulfonyl Azide in Pyridines.

A. In 2-Picoline.—A stirred solution of benzenesulfonyl azide (6.1 g) in freshly distilled 2-picoline (156 g) was heated in an oil bath at 125–130° until no more nitrogen was evolved (48 hr). The excess 2-picoline was distilled *in vacuo* and the pasty black residue was chromatographed on a column (2.5 × 30 cm) of silica gel (60–200 mesh). Elution with light petroleum ether (bp 30–60°)–ether (5:1 and then 1:1, v/v) gave benzenesulfonamide (2.31 g, 45%), mp 152–154° (from aqueous EtOH). Elution with ether gave a mixture of 3- and 5-benzenesulfonamido-2-methylpyridine (0.72 g, 8.7%). Fractional crystallization from benzene–methanol and benzene–chloroform gave **5-benzenesulfonamido-2-methylpyridine**, mp 181–182° (from benzene–MeOH), as the insoluble fraction, followed by 3-benzenesulfonamido-2-methylpyridine, mp 146–148° (from benzene–acetone) (insufficient quantities of pure material to permit analysis, but structure confirmed by nmr and mass spectroscopy). The 2,5 isomer was identical with an authentic sample prepared from 5-amino-2-picoline and benzenesulfonyl chloride: mass spectrum *m/e* (rel intensity) 248 (30, M^+), 107 (100) ($M^+ - C_6H_5SO_2$), 80 (16, $M^+ - C_6H_5SO_2 - HCN$), 77 (50, Ph), 53 (60), 52 (23), 51 (39), 39 (16).

Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87. Found: C, 57.67; H, 4.56.

Elution with $CHCl_3$–MeOH (10:1, v/v) gave **1-benzenesulfonylimino-2-methylpyridinium ylide** (3.07 g, 37%), which was purified for analysis by preparative thin layer chromatography on silica gel PF_{254} (Merck AG) [developed with $CHCl_3$–MeOH (10:1, v/v)] and recrystallization from benzene–$CHCl_3$ to give colorless crystals, mp 153–155°, identical with an authentic sample prepared as outlined below.

Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87. Found: C, 58.18; H, 5.04.

Elution with MeOH gave a brown pasty product (0.31 g) which was not investigated further.

B. In 2,6-Lutidine.—The decomposition of benzenesulfonyl azide (40 g) in freshly distilled 2,6-lutidine (70 g) was carried out and worked up as described above for 2-picoline. Elution of the silica gel column with light petroleum ether (bp 60–90°)–ether (10:1, v/v) gave a product (15 mg), mp 111–112° (from light petroleum ether), mass spectrum *m/e* (rel intensity) 210 (16, M^+), 209 (100, $M^+ - 1$), which is probably 1,2-bis(6-methyl-2-pyridyl)ethylene. Elution with benzene–ether (1:1, v/v) afforded benzenesulfonamide (1.92 g, 57%), mp 152–154°. Elution with ether gave **3-benzenesulfonamido-2,6-dimethylpyridine** (0.765 g, 13%), mp 155.5–156.5° (from benzene–CCl_4), identical in all respects with a sample synthesized from 3-amino-2,6-lutidine and benzenesulfonyl chloride in pyridine: mass spectrum *m/e* (rel intensity) 262 (18, M^+), 121 (100, $M^+ - C_6H_5SO_2$), 94 (23, $M^+ - C_6H_5SO_2 - HCN$), 77 (14), 53 (39), 43 (27).

Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.52; H, 5.38. Found: C, 59.86; H, 5.54.

Elution with $CHCl_3$–MeOH (10:1, v/v) gave **1-benzenesulfonylimino-2,6-dimethylpyridinium ylide** (1.0 g, 18%), mp 172–176°, which, after purification by tlc, had mp 177° (benzene–EtOH).

Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.52; H, 5.38. Found: C, 59.17; H, 5.54.

Elution with methanol gave black tarry material (0.17 g).

C. In 3-Picoline.—The reaction was carried out as above to give benzenesulfonamide (23%) and **1-benzenesulfonylimino-3-methylpyridinium ylide** (49%), mp 165–166° (benzene–ethyl acetate).

Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87. Found: C, 58.02; H, 4.79.

Methanol eluted a brown tar (1.3 g).

D. In 4-Picoline.—Carried out as above the reaction yielded benzenesulfonamide (62%) and **3-benzenesulfonamido-4-methylpyridine** (5%): mp 185–186° (benzene–EtOH); mass spectrum *m/e* (rel intensity) 248 (30, M^+), 107 (100, $M^+ - C_6H_5SO_2$), 80 (19, $M^+ - C_6H_5SO_2 - HCN$), 77 (25), 53 (48), 51 (25).

Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87. Found: C, 58.22; H, 4.90.

Elution with Et_2O–CH_2Cl_2 gave **1-benzenesulfonylimido-4-methylpyridinium ylide** (18%), mp 138–139° (benzene–ethyl acetate).

Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87. Found: C, 58.01; H, 4.84.

Elution with methanol gave a brown, intractable solid, mp >280°.

E. In 3,5-Lutidine.—Two products were obtained: benzenesulfonamide (37%) and **1-benzenesulfonylimido-3,5-dimethylpyridinium ylide** (54%), mp 211–212° (benzene–EtOH), identical with an authentic sample prepared from 1-amino-3,5-dimethylpyridinium iodide and benzenesulfonyl chloride in the presence of aqueous KOH.

Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.52; H, 5.38. Found: C, 59.30; H, 5.54.

F. In 2,4,6-Trimethylpyridine.—From the decomposition of benzenesulfonyl azide (6.1 g) in 2,4,6-collidine (200 g) there was obtained a product (59 mg) of unknown structure, mp 54–58°, M^+ 218 [eluted with light petroleum ether (10:1, v/v)]. Elution with light petroleum ether (1:1, v/v) gave **3-benzenesulfonamido-2,4,6-trimethylpyridine** (1.11 g, 12%), mp 127–128° (cyclohexane), identical with an authentic sample prepared from 3-amino-2,4,6-collidine and benzenesulfonyl chloride in pyridine: mass spectrum *m/e* (rel intensity) 276 (14, M^+), 135 (100, $M^+ - C_6H_5SO_2$), 108 (30, $M^+ - C_6H_5SO_2 - HCN$), 77 (7), 67 (21), 41 (14).

Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84. Found: C, 60.78; H, 5.89.

Elution with petroleum ether–ether (1:3, v/v) and then ether gave benzenesulfonamide (3.51 g, 61%). Elution with $CHCl_3$ gave **1-benzenesulfonimido-2,4,6-trimethylpyridinium ylide** (1.41 g, 15%), mp 145° after purification by preparative tlc and recrystallization from benzene. The product was identical with that obtained from 2,4,6-trimethylpyrylium perchlorate and benzenesulfonylhydrazide as described below.

Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84. Found: C, 60.68; H, 6.15.

A black, gummy tar (0.37 g) was obtained on elution with MeOH.

G. In 4-Cyanopyridine.—A mixture of 4-cyanopyridine (25 g) and benzenesulfonyl azide (9.2 g) was stirred and heated to 110° (the mixture became homogeneous at 60°) and kept at 110–120° until N_2 evolution ceased (50 hr). The excess cyanopyridine was mostly removed by vacuum distillation and the residue was chromatographed on a column (2.5 × 30 cm) of basic alumina. Elution with light petroleum ether (1:1, v/v) gave unchanged 4-cyanopyridine (3.7 g). Elution with ether gave benzenesulfonamide (2.36 g, 30%), while elution with chloroform gave **1-benzenesulfonylimino-4-cyanopyridinium ylide** (2.22 g, 17%): mp 160–161° (from benzene–cyclohexane); ir (KBr) 2250 cm^{-1} (C≡N); mass spectrum *m/e* 259 (M^+); nmr τ 1.17 (dd, $J_{2,3}$ = 7, $J_{2,4}$ = 1.5 Hz, 2 H, C_2 H, C_6 H), 1.82 (dd, $J_{3,4}$ = 7.5, $J_{2,4}$ = 1.5 Hz, 2 H, C_3 H, C_5 H), 2.21 (dd, 2 H, ortho CH), 2.51 (m, 4 H, meta CH, para CH).

Anal. Calcd for $C_{12}H_9N_3O_2S$: C, 55.72; H, 3.50. Found: C, 55.83; H, 3.58.

***N*-Benzenesulfonyliminoacridinium Ylide.**—A mixture of

(17) "Dictionary of Organic Compounds," 4th ed, Vol. 4, Eyre and Spottiswoode, 1965.

(18) E. C. Taylor, Jr., and N. W. Kalenda, *J. Amer. Chem. Soc.*, **76**, 1699 (1954).

(19) E. Plazek, *Ber.*, **72**, 577 (1939).

acridine (18 g) and benzenesulfonyl azide (9 g) was heated and stirred at 125–130° for 50 hr. The tacky mixture was dissolved in hot MeOH, and the solution was concentrated and chromatographed on alumina (2.5 × 70 cm). Elution with light petroleum and with light petroleum ether (1:1, v/v) gave acridine (1.60 g). Elution with ether gave the ylide (335 mg, 2%): mp 211–212° (from benzene–cyclohexane); ir (KBr) 3180 (w), 3060 (w), 1530 (w), 1460 (m), 1420 (m), 1360 (s), 1295 (m), 1285 (w), 1165 (s), 1135 (w), 1095 (s), 1075 (w), 1045 (m), 950 (s), 910 (s), 880 (w), 850 (m), 810 (w), 750 (s), and 685 cm^{-1} (s); mass spectrum *m/e* (rel intensity) 334 (35, M^+), 270 (6), 194 (16), 193 (100), 167 (9), 166 (45), 140 (8), 77 (7).

Anal. Calcd for $C_{19}H_{14}N_2O_2S$: C, 68.25; H, 4.22. Found: C, 68.38; H, 4.31.

Elution with ether–chloroform (8:2, v/v) gave benzenesulfonamide (350 mg, 4.5%).

1-Methanesulfonyliminopyridinium Ylide. A. From 1-Aminopyridinium Salt.—A solution of hydroxylamine-*O*-sulfonic acid (5.7 g) in water (50 ml) was neutralized with KOH (2.8 g) in water (10 ml) at 5°, and the resulting solution was added dropwise to pyridine (20 g) at 70–80°. The solution was kept at that temperature for another 30 min and K_2CO_3 (7 g) was then added with cooling. Water and pyridine were evaporated below 40° and the residue was dissolved in ethanol (150 ml). The inorganic salts were filtered. K_2CO_3 (10 g) was added to the filtrate and, after 1 hr, methanesulfonyl chloride (5.8 g) was added and the solution was stirred at room temperature for 12 hr. It was filtered, the filtrate was concentrated *in vacuo*, and the residue was chromatographed on a column of alumina. Elution with $CHCl_3$ gave the ylide (1.66 g, 19%): mp 177–178° (EtOH–ethyl acetate); ir (KBr) 3100 (w), 3080 (w), 3050 (w), 3000 (w), 2920 (w), 1612 (m), 1475 (s), 1430 (w), 1330 (w), 1270 (s), 1160 (m), 1115 (s), 1080 (m), 1030 (w), 920 (s), 810 (s), 785 (m), 725 (w), and 690 cm^{-1} (s); λ_{max}^{EtOH} 245 nm (ϵ 8300), 308 (2000); mass spectrum *m/e* (rel intensity) (30, M^+); nmr (DMSO-d_6) τ 1.03 (dd, $J_{2,3}$ = 7, $J_{2,4}$ = 1.3 Hz, 2 H, C_2 H and C_6 H), 1.51 (m, $J_{3,4}$ = 6.5, $J_{2,4}$ = 1.3 Hz, 1 H, C_4 H), 1.87 (dd, $J_{2,3}$ = 7, $J_{3,4}$ = 6.5 Hz, 2 H, C_3 H and C_5 H) and 7.11 (s, 3 H, CH_3).

Anal. Calcd for $C_6H_8N_2O_2S$: C, 41.85; H, 4.68. Found: C, 42.03; H, 4.74.

B. From Methanesulfonyl Azide.—A solution of methanesulfonyl azide (9.0 g) in dry pyridine (30 g) was boiled under reflux for 30 hr, the excess pyridine was distilled *in vacuo*, and the black residue was chromatographed on a column of basic alumina (3 × 40 cm) to give methanesulfonamide (4.97 g, 70%), mp 91.5–92.5°, and 1-methanesulfonyliminopyridinium ylide (0.38 g, 3%), mp 175°, identical with the sample obtained above.

3-Benzenesulfonamido-2,4,6-trimethylpyridine.—Benzenesulfonyl chloride (1.96 g) was added dropwise to a solution of 3-amino-2,4,6-collidine (1.36 g) in dry pyridine (5 ml) below 45°, and the solution was then heated on a steam bath for 40 min. Aqueous NaOH (3%, 10 ml) was added and the mixture was heated for 20 min. The solvent was evaporated and the residue was triturated with water (10 ml) to give the sulfonamide (1.47 g, 53%), mp 128° (from benzene–cyclohexane).

3-(*N*,*N*-Dibenzenesulfonyl)amino-2,4,6-trimethylpyridine.—A solution of the amine (0.61 g) and benzenesulfonyl chloride (1.0 g) in dry pyridine (5 ml) was boiled under reflux for 20 min. Aqueous NaOH (3%, 10 ml) was added and the mixture was heated for 20 min. The solvent was evaporated and the yellow residue (0.90 g, 45%) was recrystallized from light petroleum ether (bp 60–90°)–benzene to give the disulfonamide: mp 168.5–169.5°; ir (KBr) 3070 (w), 3030 (w), 2970 (w), 2940 (w), 1600 (s), 1550 (w), 1480 (w), 1450 (s), 1360 (s), 1300 (w), 1220 (m), 1165 (s), 1080 (s), 1025 (w), 955 (w), 930 (w), 905 (m), 880 (s), 855 (w), 760 (m), 750 (s), 730 (s), 720 (m), 715 (s), 685 (s), and 640 cm^{-1} (s); nmr τ 8.17 (s, 3 H, CH_3), 8.00 (s, 3 H, CH_3), 7.53 (s, 3 H, CH_3), 2.32–2.56 (m, 6 H, meta and para ArH), 2.13 (s, 1 H, C_5 H), 1.95 (dd, ortho, meta J = 8 Hz, ortho, para J = 2 Hz, 4 H, ortho ArH); mass spectrum *m/e* 275 (M^+).

Anal. Calcd for $C_{20}H_{20}N_2O_4S_2$: C, 57.67; H, 4.85. Found: C, 57.42; H, 4.70.

2-Benzenesulfonamido-6-methylpyridine.—Prepared from 2-amino-6-methylpyridine and benzenesulfonyl chloride in dry pyridine on a steam bath, it was obtained in 87% yield: mp 139–140°; ir (KBr) (main peaks only) 3225 (m), 1610 (s), 1530 (s), 1370 (s), 1270 (s), 1135 (s), 1090 (s), 855 (s), 790 (s), 770 (s), 745 (s), 710 (m), and 700 cm^{-1} (s); mass spectrum *m/e* 248 (M^+).

Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87. Found: C, 58.16; H, 4.99.

1-Benzenesulfonyliminopyridinium Ylide.—This was prepared in 84% yield from 1-aminopyridinium iodide, potassium carbonate, and benzenesulfonyl chloride, mp 154–155°. It was identical with the product obtained from the thermolysis of benzenesulfonyl azide in pyridine.

1-Benzenesulfonylimino-2-methylpyridinium Ylide.—An ice-cold solution of 1-amino-2-methylpyridinium iodide[20] (0.472 g) in water (10 ml) was basified at 0–5° with solid K_2CO_3 and this solution was added portionwise to a solution of benzenesulfonyl chloride (0.360 g) in dry acetone (10 ml). After stirring the solution at room temperature overnight the acetone was evaporated and the solid was filtered. Recrystallization from benzene–methylene chloride gave the ylide (0.240 g, 49%), mp 154–155°, identical with the product obtained from 2-picoline and the sulfonyl azide.

1-Benzenesulfonylimino-2,4,6-trimethylpyridinium Ylide.—A mixture of 2,4,6-trimethylpyrylium perchlorate[21] (2.22 g) and benzenesulfonylhydrazide (1.72 g) was boiled under reflux in absolute EtOH (60 ml) for 12 hr. Unreacted pyrylium salt was filtered from the hot solution, which was then concentrated *in vacuo* to give 1-benzenesulfonamido-2,4,6-trimethylpyridinium perchlorate (2.20 g, 60%): mp 116–120°; ir (KBr) (main peaks only) 2700–2600 (br m), 1600 (s), 1430 (s), 1330 (s), 1160–1060 (br s), 855 (br s), 750 (m), 715 s, 680 (s), and 620–550 cm^{-1} (br s).

The perchlorate (1.88 g) was dissolved in methanol (20 ml), the ice-cold solution was added portionwise to KOH (2 g) in water (7 ml), and methanol (10 ml) was then added. Potassium perchlorate precipitated and was filtered, and the filtrate was evaporated to dryness. The residue was chromatographed on a column of basic alumina (1.5 × 20 cm). Elution with $CHCl_3$ gave the desired ylide (1.32 g), mp 145–146°.

Reaction of Benzenesulfonyl Azide with Quinoline.—A mixture of quinoline (7.80 g) and benzenesulfonyl azide (5.49 g) was heated in an oil bath at 125° with stirring for 65 hr. The product was chromatographed on basic alumina (3 × 30 cm). Elution with light petroleum ether–ether (9:1, v/v) gave diphenyl disulfide (56 mg), mp 60°, identical with an authentic sample. Elution with light petroleum ether–ether (3:7, v/v) gave **8-benzenesulfonamidoquinoline** (280 mg, 1%), mp 134–135° (CCl_4), identical with a sample prepared in 99% yield from 8-aminoquinoline and benzenesulfonyl chloride in pyridine on a steam bath: ir (KBr) (main peaks only) 3200 (m, NH), 1360 (s), 1308 (s), 1170 (s), 1095 (s), 980 (s), 860 (s), 825 (m), 793 (s), 755 (s), 725 (s), and 691 cm^{-1} (s); mass spectrum *m/e* (rel intensity) (19, M^+), 220 (49), 219 (33), 143 (100), 116 (60), 89 (22), 77 (28), 63 (13), 51 (22), and 39 (17); nmr τ 1.34 (dd, $J_{2,3}$ = 4.5 Hz, $J_{2,4}$ = 1.8 Hz, 1 H, C_2 H), 2.01 (dd, $J_{3,4}$ = 8.5, $J_{2,4}$ = 1.8 Hz, 1 H, C_4 H), 2.19 (dd, ortho, meta J = 9.5, ortho, para J = 2.0 Hz, 2 H, ortho CH), 2.21 (dd, $J_{5,6}$ = 8.5, $J_{5,7}$ = 1 Hz, 1 H, C_5 H), and 2.63–2.79 (m, 6 H, C_3 H, C_6 H, C_7 H, meta CH, para CH).

Anal. Calcd for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.16. Found: C, 63.47; H, 4.36.

Elution with petroleum ether–ether (1:9, v/v) gave benzenesulfonamide (1.41 g, 30%). Elution with $CHCl_3$ gave **1-benzenesulfonyliminoquinolinium ylide** (1.019 g, 12%), mp 183° (ethyl acetate–ethanol), identical with an authentic sample prepared as described below: ir (KBr) (main peaks only) 1296 (s), 1218 (s), 1140 (s), 1092 (s), 927 (s), 836 (s), 817 (m), 774 (s), 737 (m), and 704 cm^{-1} (m); mass spectrum *m/e* 284 (21, M^+); nmr τ 0.91 (dd, $J_{2,3}$ = 6, $J_{2,4}$ = 1 Hz, 1 H, C_2 H), 1.51 (overlapping dd, J = 7, 1 Hz, 2 H, C_4 H and C_8 H); λ_{max}^{EtOH} 365 nm (infl, ϵ 2500), 324 (6000), 293 (infl, 2000), 259 (infl, 5900), 234 (31,900).

Anal. Calcd for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.16. Found: C, 63.33; H, 4.37.

Elution with MeOH gave black, gummy material (2.04 g) which was not investigated further.

1-Benzenesulfonyliminoquinolinium Ylide.—A solution of hydroxylamine-*O*-sulfonic acid (20 g) and potassium hydroxide

(20) R. Gösl and A. Meuwsen, *Chem. Ber.*, **92**, 2523 (1959).

(21) G. N. Derofenko and S. V. Krivun, *Metody Poluch. Khim. Reaktivov Prep.*, No. 17, 149 (1967); *Chem. Abstr.*, **71**, 61161 (1969); O. Diels and K. Alder, *Ber.*, **60**, 716 (1927).

(10 g) in water (60 ml) was added to quinoline (45 g) at 70–80°, and the reaction mixture was stirred for another 30 min at that temperature. A solution of potassium carbonate (12 g) in water (40 ml) was added, and the mixture was washed with ether (2 × 100 ml) and concentrated to a small volume below 40°. Potassium carbonate (30 g) and ethanol (200 ml) were added, the mixture was stirred at room temperature for 1 hr, and then benzenesulfonyl chloride (34 g) was added. After the mixture was stirred overnight at room temperature, the inorganic solids were filtered, and the filtrate was concentrated and chromatographed on a column (3 × 30 cm) of basic alumina. Elution with $CHCl_3$ gave the ylide (10.86 g, 20%), mp 183°.

5-Benzenesulfonamidoquinoline.—This was prepared from 5-aminoquinoline (0.5 g) and benzenesulfonyl chloride (0.5 g) in pyridine (2 ml) to give the sulfonamide (0.70 g): mp 207–208° (ethyl acetate); mass spectrum *m/e* (rel intensity) 284 (24, M^+), 143 (100), 116 (70), 89 (30), 77 (33), 63 (14), 51 (23), 40 (20), 39 (15); ir (KBr) (main peaks only) 2670 (br w), 1394 (s), 1336 (br s), 1170 (s), 1094 (s), 810 (s), 770 (s), and 735 cm^{-1} (m).

Anal. Calcd for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.16. Found: C, 63.10; H, 4.40.

Reaction of Benzenesulfonyl Azide with Isoquinoline.—The reaction was carried out as described for quinoline above; 51.7% of the isoquinoline was recovered; and benzenesulfonamide (51%) was also obtained. The remainder of the products resembled black coal.

Reaction of Benzenesulfonyl Azide with 3-Methylisoquinoline.—3-Methylisoquinoline (21.45 g) was heated with benzenesulfonyl azide (5.49 g) at 125–130° for 12 hr. The isoquinoline (16.55 g) was recovered. Chromatography on basic alumina and elution with petroleum ether–ether (2:8, v/v) gave benzenesulfonyl azide (112 mg). Elution with ether gave benzenesulfonamide (1.245 g, 27.6%). Elution with $CHCl_3$ gave **2-benzenesulfonylimino-3-methylisoquinolinium ylide** (1.790 g, 20.9%): mp 210–211° (benzene–ethyl acetate); ir (KBr) (main peaks only) 1294 (s), 1280 (s), 1265 (s), 1145 (s), 1090 (s), 940 (s), 770 (s), 757 (s), 721 (m), and 700 cm^{-1} (m); mass spectrum *m/e* (rel intensity) 298 (20, M^+); nmr τ 0.56 (s, 1 H, C_1 H), other aromatic C H's, complex multiplets at 1.95–2.75, 7.57 (s, 3 H, CH_3).

Anal. Calcd for $C_{16}H_{14}N_2O_2S$: C, 64.41; H, 4.70. Found: C, 64.50; H, 4.91.

Elution with ethyl acetate gave **4-benzenesulfonamido-3-methylisoquinoline** (1.06 g, 12.4%): mp 234.5–235° (benzene–ethanol); ir (KBr) 3265 (s, NH), 3100–3050 (w), 1620 (m), 1578 (m), 1480 (w), 1450 (s), 1430 (w), 1385 (s), 1325 (s), 1250 (m), 1180 (m), 1165 (s), 1042 (s), 968 (w), 926 (m), 905 (w), 870 (m), 794 (s), 780 (m), 762 (s), 740 (w), 728 (m), 696 (m), and 670 cm^{-1} (w); mass spectrum *m/e* (rel intensity) 298 (12, m^+), 157 (100), 103 (17), 89 (30), 77 (24), 63 (11), 51 (15), 44 (16), 39 (13); nmr (DMSO-d_6) τ 0.56 (s, 1 H, C_1 H), 1.65 (md, $J_{7,8}$ = 7 Hz, C_8 H), 2.00–2.20 (m, 9 H), and 7.45 (s, 3 H, CH_3).

Anal. Calcd for $C_{16}H_{14}N_2O_2S$: C, 64.41; H, 4.70. Found: C, 64.29; H, 4.91.

Elution with methanol gave a black, intractable solid (1.5 g).

5-Benzenesulfonamido-3-methylisoquinoline.—5-Amino-3-methylisoquinoline (1.60 g) and benzenesulfonyl chloride (2.00 g) were heated on a steam bath for 1 hr, NaOH (0.6 g) in water (3 ml) was added, and heating was continued for 10 min. The solution was evaporated to dryness and the residue was triturated with water (15 ml) to give the desired sulfonamide (2.08 g, 70%): mp 195–196° (ethyl acetate); ir (KBr) (main bands only) 2780 (br m), 2730 (br m), 1630 (s), 1590 (s), 1430 (br s), 1330 (br s), 1160 (br s), 1087 (s), 916 (s), 880 (s), 735 (br s), and 690 cm^{-1} (br s); mass spectrum *m/e* (rel intensity) 298 (14, M^+), 157 (100), 130 (20), 77 (34), 51 (17), 45 (11); the compound was too insoluble in $CDCl_3$, $(CD_3)_2CO$, and DMSO-d_6 to permit the determination of its nmr spectrum.

Anal. Calcd for $C_{16}H_{14}N_2O_2S$: C, 64.41; H, 4.70. Found: C, 64.23; H, 4.79.

1,2,3-Triazolo[1,5-*a*]quinoline.—A solution of benzenesulfonyl azide (5.49 g) in quinaldine (25 g) was stirred and heated at 110–115° for 40 hr. The excess quinaldine (18 g) was distilled off at 1 mm below 100°, and the residue was dissolved in methylene chloride and chromatographed on a column of alumina (3 × 40 cm). Elution with petroleum ether–ether (1:1, v/v) gave the triazoloquinoline (3.60 g, 72%): mp 81.5–82° [from ether–light petroleum ether (bp 60–80°)] (lit.[14] mp 81°); ir (KBr) (main bands only) 1613 (s), 1468 (s), 1450 (s), 1398 (s), 1285 (s), 1143 (s), 1107 (s), 975 (s), 817 (s), 800 (m), and 750 cm^{-1} (s); λ_{max}^{EtOH} 246 nm (ϵ 16,900), 252 (16,300), 261 (9600), 287 (6500), 295 (6900), 316 (6300), 330 (5900); mass spectrum *m/e* (rel intensity) 169 (42, M^+), 141 (100, $M^+ - N_2$), 140 (68), 114 (53), 88 (15), 63 (21), 41 (23), 39 (16); nmr τ 1.28 (d, $J_{7,8}$ = 8 Hz, 1 H, C_9 H), 1.96 (s, 1 H, C_3 H), 2.20–2.56 (m, 5 H).

Anal. Calcd for $C_{10}H_7N_3$: C, 70.99; H, 4.17; N, 24.84. Found: C, 70.90; H, 4.34; N, 24.89.

Elution with petroleum ether–ether (1:9, v/v) gave benzenesulfonamide (4.20 g, 89%). A similar result was obtained when the thermolysis was carried out at 125–130°.

1,2,3-Triazolo[5,1-*a*]isoquinoline.—A mixture of 1-methylisoquinoline (4.29 g) and benzenesulfonyl azide (5.49 g) was heated at 125° for 20 hr and worked up as described for quinaldine above. Elution of the column with light petroleum ether–ether (8:2, v/v) gave diphenyl disulfide (80 mg), mp 59–60°, identical with an authentic sample. Further elution with this solvent afforded **1,2,3-triazolo[5,1-*a*]isoquinoline** (2.881 g, 64%): mp 110–111° (benzene–cyclohexane); ir (KBr) (main bands only) 3105 (w), 1395 (s), 1205 (s), 968 (s), 838 (s), 806 (s), 775 (s), 763 (w), 753 (m), and 695 cm^{-1} (w); mass spectrum *m/e* (rel intensity) 169 (42, M^+), 141 (100, $M^+ - N_2$), 140 (74), 114 (70), 113 (27), 88 (20), 87 (14), 63 (27), 62 (26), 51 (17), 50 (16), 39 (22); nmr τ 1.64 (d, $J_{4,5}$ = 8 Hz, 1 H, C_4 H), 1.70 (s, 1 H, C_1 H), 2.07 (d, $J_{8,9}$ = 6 Hz, 1 H, C_9 H), 2.53 (dd, $J_{8,9}$ = 6, $J_{7,8}$ = 5.5 Hz, 1 H, C_8 H) 2.32–2.46 (m, 2 H, C_6 H and C_7 H), 2.98 (d, $J_{4,5}$ = 8 Hz, 1 H, C_5 H); λ_{max}^{EtOH} 241 nm (ϵ 34,400), 248 (33,500), 255 (25,000), 299 (2100), 306 (2000), 313 (3400), 327 (3400).

Anal. Calcd for $C_{10}H_7N_3$: C, 70.99; H, 4.17. Found: C, 71.15; H, 4.32.

Elution with $CHCl_3$ gave benzenesulfonamide (4.332 g, 92%).

1,2,3-Triazolo[1,5-*f*]phenanthridine.—6-Methylphenanthridine (2.90 g) and benzenesulfonyl azide (2.75 g) were heated at 125° for 15 hr and worked up as described above for quinaldine. Elution of the column with light petroleum ether–ether (5:1, v/v) gave unchanged 6-methylphenanthridine (77 mg, 2.6%). Elution with light petroleum ether–ether (4:1, v/v) gave the triazolophenanthridine (2.797, 88%): mp 187–188° (benzene–cyclohexane); ir (KBr) (main peaks only) 3115 (w), 1460 (s), 1445 (s), 1050 (m), 825 (m), 753 (s), and 724 cm^{-1} (s); mass spectrum *m/e* (rel intensity) 219 (31, M^+), 191 (83), 190 (100, $M^+ - N_2 - H$), 164 (27), 163 (24), 95 (15), 82 (29), 81 (20), 69 (21), 63 (22), 57 (22), 55 (25), 51 (15), 50 (15), 43 (22), 41 (29), 39 (34); nmr τ 0.92 (d, $J_{10,11}$ = 5 Hz, 1 H, C_{11} H), 2.51 (s, 1 H, C_3 H); λ_{max}^{EtOH} 243 nm (infl, ϵ 45,000), 248 (50,000), 299 (5000), 306 (4500), 312 (4700), 319 (2800), 327 (4700).

Anal. Calcd for $C_{14}H_9N_3$: C, 76.70; H, 4.13. Found: C, 76.85; H, 4.28.

Elution with ether gave benzenesulfonamide (2.30 g, 99%).

Registry No.—**4,** 34456-51-4; **5b** (2,3 isomer), 34456-52-5; **5b** (2,5 isomer), 34456-53-6; **5c,** 34456-54-7; **5f,** 34456-55-8; **5g,** 34456-56-9; **6a,** 28460-28-8; **6b,** 34456-58-1; **6c,** 34456-59-2; **6d,** 34456-60-5; **6e,** 34456-61-6; **6f,** 34456-62-7; **6g,** 34456-63-8; **6h,** 34456-64-9; **15,** 34456-65-0; **16,** 16082-59-0; **17,** 34456-67-2; **18,** 235-21-2; **24,** 34456-69-4; **25,** 34456-70-7; **28,** 34456-71-8; **29,** 34456-72-9; 1,2-bis(6-methyl-2-pyridyl)ethylene, 34456-73-0; methanesulfonamide, 3144-09-0; 3-(*N*,*N*-dibenzenesulfonyl)amino-2,4,6-trimethylpyridine, 34456-74-1; 2-benzenesulfonamido-6-methylpyridine, 34456-75-2; 5-benzenesulfonamidequinoline, 34298-61-8; 5-benzenesulfonamido-3-methylisoquinoline, 34456-77-4.

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