Table V. Rate Constants for Isomerization of 2,4,6-Tris(perdeuterio-*tert*-butyl)phenyl in *tert*-Butylbenzene

T, K	P, atm	$\log k_{1,1}$, s^{-1}
251	1	−0.352
251	290	−0.392
253	1	−0.340
253	300	−0.306
258	1	−0.094
258	295	−0.099
263	1	0.004
263	300	0.009
269	1	0.255
269	295	0.262
280	1	0.549
280	300	0.587
289	1	0.865
289	290	0.873

testing of the relationship between $\Delta V_{11(H)}^{\ddagger}$ and $\Delta V_{11(D)}^{\ddagger}$ shows that the probability that these volumes of activation are different is >99%. We take this to be further evidence supporting the hypothesis that the isomerization of 2,4,6-tri-*tert*-butylphenyl proceeds by quantum mechanical tunneling.

We believe that these experiments were probably more difficult to carry out than would be the case for most reactions purported to involve tunneling. That is, most purported examples of reactions which involve tunneling take place on reasonably long time scales (minutes or more) and do not require that the reagents be photogenerated within an EPR cavity. Instead, these reactions can usually be monitored with existing apparatus up to pressures of several kilobars. Since volumes of activation can provide additional evidence supporting or denying the involvement of tunneling, we strongly advocate their measurement whenever possible.

Acknowledgment. We would like to thank W. J. LeNoble and P. Staub for providing us with detailed drawings of their pressure apparatus, J. Vandenhoff for patient and skillful glass blowing, and G. O. Grummett and C. Pink for their help in the design and construction of the coupler.

Supplementary Material Available: Rate constants for the isomerization of tris(perdeuterio-*tert*-butyl)phenyl in cyclopropane solvent (1 page). Ordering information is given on any current masthead page.

The Decomposition of β-Phenethylsulfonyl Azides. Solution Chemistry and Flash Vacuum Pyrolysis[1]

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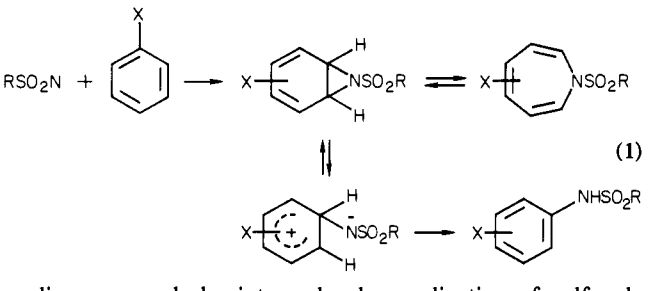
Abstract: The intramolecular cyclization of the parent title compound and a number of para-substituted derivatives (**1**) in solution was found to take place in low yield and to be accompanied by products of intermolecular reactions, namely, C–H insertion (**4**) and hydrogen abstraction (**3**). The use of an excess of a relatively inert solvent Freon 113 led to a better yield of the desired 3,4-dihydro-2,1-benzothiazine 2,2-dioxides (**2**). Flash vacuum pyrolysis (FVP) of **1** at 250–300 °C also gave some **2**, but the use of higher temperatures led to the formation of styrenes (**8**), indolines (**9**), indoles (**10**), sulfur dioxide, and the remarkable transformation products, the 4-substituted 6,7-dihydro-5*H*-1-pyrindines (**7**), in good yield. The styrenes result from the elimination of HN_3 and SO_2 from the azides, and indolines are formed in good yield by FVP of **2** at 650 °C. The dihydropyrindines are not obtained from **2**, and β-phenethylnitrene is not a source of any of the above observed products. A mechanism is proposed for the formation of **7** from β-arylethylsulfonylnitrenes. Consistent with this mechanism is the observation that both 1- and 2-phenylpropanesulfonyl azide give a mixture of 6- and 7-methyl-6,7-dihydro-5*H*-1-pyrindines in the same ratio on FVP at 650 °C. Thermolysis of **1a** in benzene at 100 °C gives an *N*-sulfonylazepine derivative. The FVP of **1** and **2** at 650 °C are preparative routes to **7** and **9**, respectively.

For a number of years we have been studying the reactions of sulfonylnitrenes, generated thermally from the corresponding azides,[3] with aromatic substrates.[4] Thus, it was established that, in the rate-determining step of the substitution process, singlet sulfonylnitrenes added to an aromatic nucleus to give a benzaziridine intermediate which underwent ring opening in a fast, product-determining step to give the *N*-sulfonanilides (thermodynamic control) or the *N*-sulfonylazepines (kinetic control) (eq 1). This reaction was then extended to the synthesis of heterocyclic compounds by intramolecular cyclization of sulfonylnitrenes.[5] Thus, cyclizations of 2-biarylsulfonyl azides[6a] and



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(1) For a preliminary communication on part of this work, see: Abramovitch, R. A.; Holcomb, W. D. *J. Am. Chem. Soc.* **1975**, *97*, 676.
(2) To whom correspondence should be addressed at Clemson University.
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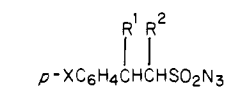
ferrocenylsulfonyl azide[6b] and intramolecular insertions of arylsulfonylnitrenes into aliphatic side chains[6c] were carried out successfully. On the other hand, no intramolecular cyclization product was found in the decomposition (thermal or photochemical) of ferrocene-1,1′-disulfonyl azide, only products of intermolecular reactions being observed.[6d]

We now report studies aimed at effecting intramolecular cyclization onto an aromatic nucleus by a sulfonylnitrene located in an aliphatic side chain. It had been shown previously that thermolysis of α-toluenesulfonyl azide in solution gave none of the desired cyclization product, only intermolecular products (insertion, hydrogen abstraction) being formed, and this was attributed[5] to strain in the required[4] fused benzaziridine intermediate. This strain should be decreased appreciably in the intermediate expected from the intramolecular addition of β-phenethylsulfonylnitrene (6-3-5 fused system as opposed to 6-3-4 in the case of the α-toluenesulfonylnitrene) so that cyclization was expected to take place in this case to give a six-membered ring sultam. In addition to the theoretical interest in this type of reaction some practical fallout was anticipated since six-membered sultams have found use as diuretics (e.g., hydrochlorothiazide)[7a] and anticonvulsants (e.g., sulthiame).[7b]

The desired β-arylethylsulfonyl azides (**1**) could be readily



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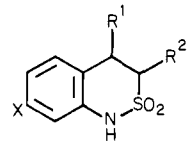

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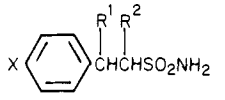

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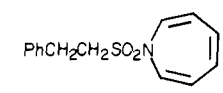

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a, X = R¹ = R² = H; b, X = Me, R¹ = R² = H; c, X = Cl, R¹ = R² = H; d, X = OMe, R¹ = R² = H; e, X = R² = H, R¹ = Me; f, X = R¹ = H, R² = Me

prepared from the corresponding sulfonyl chlorides, in turn made from the sodium sulfonates (see Experimental Section). Thermolysis of **1a** in *n*-tetradecane at 149 °C gave the desired (known[8]) sultam **2a** (6–8%), together with β-phenethylsulfonamide (**3**) (6–7%), and a mixture of isomeric *N*-tetradecyl-β-phenethylsulfonamides (47%).[1] A similarly low yield of **2** was obtained (71%) when **1a** was thermolyzed in cyclohexane at 135 °C; the main product was *N*-cyclohexyl-β-phenethylsulfonamide (**4**) (50%) (insertion by the nitrene into a C–H bond). Some **3a** (6.5%) (hydrogen abstraction) was also formed. Decomposition of **1a** in benzene at 135 °C gave **2a** (6.5%), together with the product of *intermolecular* addition to an aromatic double bond, namely, *N*-phenyl-β-phenethylsulfonamide (**5**) (5.8%), as well as **3a** (6.8%). In addition, however, the product of intermolecular addition followed by ring expansion, *N*-(β-phenethylsulfonyl)azepine (**6**), was formed (4.2%), together with what appears to be a dimer thereof (2.8%). Azepine **6** was light sensitive and could not be purified sufficiently to give satisfactory microanalytical data. Its structure assignment is based on its infrared, NMR, and low-resolution mass spectra. Formation of an *N*-sulfonylazepine under thermolytic conditions at or above 100 °C is unusual and, to our knowledge, has only been observed once before and that is the case of the decomposition of ferrocene-1,1′-disulfonyl azide in benzene at 100 °C.[6d] Thus, in this reaction, the total yield of *intermolecular* addition to an aromatic double bond is greater than that of intramolecular addition, giving a clear-cut indication of the strain involved in going to the transition state for the latter process. Hence, while the latter is strongly favored by entropy, intermolecular addition competes very effectively. Decomposition of **1a** in diglyme at 149 °C gave **2a** (6%) and appreciable quantities of **3a** (30.6%), together with SO_2 (10%). The latter was detected in every thermolysis but was measured quantitatively only in this case.

It is obvious from the above results that intermolecular processes (nitrene reacting either with solvent or with excess azide) compete successfully with the desired intramolecular reaction, thus resulting in substantially lower yields of the target sultam. Clearly, reactive solvent molecules must be removed, and the molecules of sulfonyl azide or of sulfonylnitrene must be well separated from each other to prevent their intermolecular interaction.

Two methods have been examined in order to achieve the above goal. In the first, the azide was dissolved in a large volume of an "inert" solvent and thermolyzed. High dilution should militate against intermolecular interactions of molecules of azide with nitrenes or of nitrenes with each other. It is doubtful that any solvent is truly "inert" toward the highly reactive nitrene intermediates. We have found Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) to be the best among those we tried. Thus, when a dilute solution of **1a** was heated in Freon 113 at 135 °C, **2a** was obtained in 28% yield, but some **3a** (12%) was still formed. The latter could arise from any traces of impurities in the Freon (which was >99% pure) or, more likely, from reaction of sulfonylnitrene with unreacted sulfonyl azide. The mechanism of hydrogen abstraction by a sulfonylnitrene is far from being known.[3,4] Most of the starting azide remained unaccounted for and must have given rise to the ubiquitous tars that were formed, presumably from the interaction of nitrene with solvent.

Since decomposition in Freon 113 solution gave the best yields of the desired sultam, all the other sulfonyl azides (**1b–f**) were also thermolyzed under the same conditions. In all cases, only sultam and primary sulfonamide were isolated, together with tars. The yields of sultams (**2**) and sulfonamides (**3**) respectively were as follows: 28%, 12% from **1a**; 38.1%, 10% from **1b**; 1.6%, 5.8% from **9c**; 39%, 15.7% from **9d**; 10.9%, 19.4% from **9e**; 24.5%, 18.9% from **9f**.

It is clear that reasonable, but not good, yields of the desired sultams can be achieved in some cases, though hydrogen abstraction products are formed in all cases in appreciable amounts. 4-Chloro-β-phenethylsulfonyl azide (**1c**) gives only a very low yield of sultam (**2c**). This does not appear to be owing to any particular instability of **2c** or of other final products which may be obtained from the azide under different conditions (vide infra), which suggests that, in solution at relatively low temperatures (135 °C), the halogen in the intermediate formed is particularly susceptible to intermolecular attack resulting in extensive tar formation.

The second method studied to improve yields of cyclized products by decreasing the opportunities for intermolecular reactions was flash vacuum pyrolysis (FVP).[9] In this technique the sample is vaporized under vacuum below its decomposition temperature and then passed rapidly (with or without a low pressure of an inert carrier gas) through a hot tube. The products are collected (or trapped) on a cold finger. Thus, the use of solvents is avoided and chances of intermolecular reactions between reactive intermediates and between reactive intermediates and substrate in the pyrolysis zone are minimized, favoring intramolecular (and also fragmentation) processes. Any reactive intermediates or unstable products that do survive the passage through the hot zone can react intermolecularly on the cold finger.

The vacuum thermolysis of sulfonyl azides has only been briefly investigated before the present work. Thermolysis of benzene-

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Table I. FVP of $ArCH_2CH_2SO_2N_3$

azide	column temp, °C	pyrolysis time, min	contact time, s	carrier gas	recovered azide, %	% yields 2	7	3	9	10	8
1a	250	270	0.20		35	5.6		6.0			
1a	300	335	0.45			12.8	6.9				
1a	350	330	0.43			9.9	15.7	4			
1a	400	355	0.37			11.3	32.7				
1a	300	270	0.45	N_2/ toluene[a]	11	19					
1a	400	65	0.36	N_2		8.1	45.6				6.4
1a	650	60	0.25	N_2			64.8		11.2	1.5	8.2
1b	400	80	0.35	N_2		13.5	45.6				5.2
1b	650	90	0.26	N_2			70.2		10	2.2	5.7
1c	400	80	0.35	N_2		2.0	33.2				3.4
1c	650	90	0.26	N_2			62.6		5.4	1.1[b]	7.7
1d	400	80	0.35	N_2		4.3	41.3				3.6
1d	650	90	0.26	N_2			24.7		<0.5		<0.5
1e	400	80	0.35	N_2		9.5	49[c]				3.5
1e	650	90	0.26	N_2			33.1[d]		6.9		5.1
1f	650	90	0.26	N_2		8.4	17.3[e]				1.4

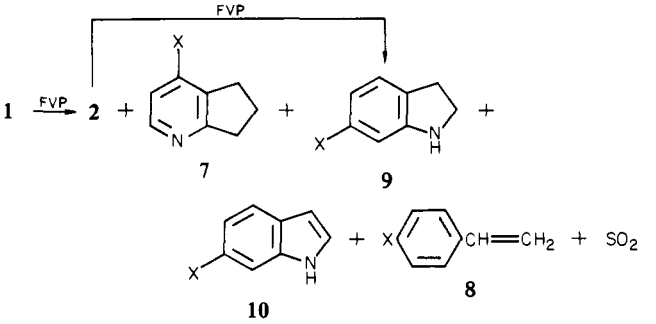
[a] No bibenzyl or toluene substitution products detected. [b] Relative molar response factor assumed to be 1.0. [c] Mixture of 11 (40% yield based on 1e) and 12 (9% yield). [d] Isolated yield of mixture of 11 (26.3%) and 12 (6.8%). [e] Isolated yield of mixture of 11 and 12 in the ratio of 4.3:1.

Table II. FVP of Substituted 3,4-Dihydro-2,1-benzothiazine 2,2-Dioxides at 650 °C

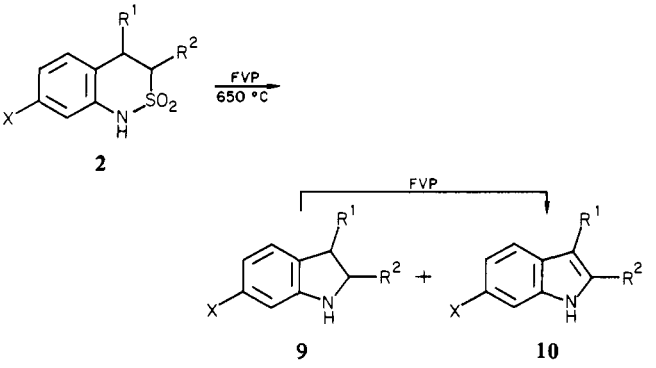
substituent	% yield indoline	indole
7-Me	88.5	2.8
7-Cl	71.2	10.8
7-OCH_3	24.7	0
4-Me	79.8	0

sulfonyl azide[10] gave some azobenzene, showing that Curtius' "starre azide" *can* undergo rearrangement to the sulfonylimine (this has also been shown to occur in solution[11]). Very soon after the publication of our first report[1] Renfrow and Devadoss[12] reported the gas-phase pyrolysis (360 °C) of benzenesulfonyl azide (both in the presence and absence of benzene as the carrier gas). The products in both cases were azobenzene (32–27%), benzenesulfonamide (2%), diphenylamine (1–3.5%), biphenyl (2–1%), and SO_2 (65–71%). Pyrolysis of 2-methylbenzenesulfonyl azide gave 2,3-dihydrobenzisothiazole 1,1-dioxide (21%) but no azobenzene derivative. On the other hand, thermolysis of this azide in benzene gave no sultam, only solvent substitution and hydrogen abstraction products being observed.

The FVP of β-phenethylsulfonyl azides (**1**) was studied both with and without an inert carrier gas flow at various temperatures. In all cases, formation of the nitrene was accompanied by competitive radical cleavage leading to the formation of sulfur dioxide.[11a,13] At the higher temperatures, loss of SO_2 occurred by another process as well which is discussed below. At 250 °C without any nitrogen carrier gas flow **1a** gave a very low yield (5.6%) of **2a** together with some **3a** (6%) and much starting azide was recovered (Table I). At 300 °C in a flow system **2a** was the only product isolated (19%) together with some starting azide (11%). Thus a threefold increase in yield of cyclization product was achieved compared to when cyclohexane, benzene, or diglyme were used as solvents in the thermolysis, but FVP is still not as good as is the use of Freon 113 as solvent in improving the cyclization yield. When the FVP was carried out at 300 °C without a carrier gas, no azide was recovered nor was any **3a** isolated. Sultam **2a** was formed in 12.8% yield. In this case, a remarkable new transformation product was isolated in low (6.9%) yield, namely, 6,7-dihydro-5*H*-1-pyrindine (**7a**). Thus the benzene ring in **1a** has been converted to a pyridine ring, and one of the aromatic carbons in **1a** has become a CH_2 group. The use of higher FVP temperatures (Table I) led to a gradual decrease in the yield of **2a** and an increase in the yield of **7a** until at 650 °C no **2a** was isolated and 64.8% of **7a** was formed; i.e., this now becomes a method of choice for the synthesis of dihydropyrindines such as **7**. At 450 °C, some styrene (**8a**) (6.4%) was formed. Slightly more (8.2%) styrene was obtained at 650 °C but, in addition, so were indoline (**9a**) (11.2%) and indole (**10a**) (1.5%). Attempts to trap intermediates by cocondensation of the FVP gases with ammonia or with aniline on the cold finger did not lead to the isolation of any meaningful quantities of any new products.



The source of the new products formed was then sought. That β-phenethylnitrene (which could result from **1a** in the gas phase by a Wolff-type rearrangement of the sulfonylnitrene following loss of SO_2[11]) did not give rise to any of the above products was shown by FVP of β-phenethyl azide: no intramolecular substitution occurred, as expected,[14] and only unidentified tars were formed. On the other hand, FVP of **2a** at 650 °C gave a good



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(12) Renfrow, W. B.; Devadoss, M. *J. Org. Chem.* **1975**, *40*, 1525.
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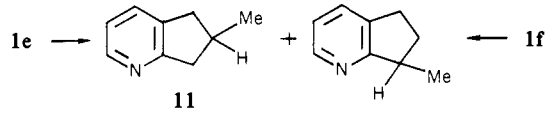
(14) Abramovitch, R. A.; Kyba, E. P. *J. Am. Chem. Soc.* **1974**, *96*, 480.

yield (75%) of indoline (**9a**) and a low yield of indole (**10a**) (7.7%). Indeed, FVP of **2** (see Table II) gave good to excellent yields of the 7-substituted indoles (except in the case of **2d** when the yield was poor). Extrusion of SO_2 from sulfones on FVP has been observed previously. Thus, dibenzylsulfones give symmetrical bibenzyls,[15] benzocyclobutene can be obtained by pyrolysis of 1,3-dihydroisothianaphthene 2,2-dioxide,[16] and loss of SO_2 from sultams has been reported.[17,18] Clearly, indoles result from the high-temperature dehydrogenation of indolines in this process, but **2** is not the source of **7** or of the styrene formed.

Additional light was thrown on the mechanism of formation of the dihydropyrindine by studying the FVP of para-X-substituted β-phenethylazides (**2b–d**). Invariably the substituent X ended up at the 4-position of the pyridine ring in **7b–d**. This was established unambiguously by NMR spectroscopy. Next, the fate of substituents in the side chain was examined. Pyrolysis of 2-phenylpropanesulfonyl azide (**1e**) gave α-methylstyrene, 3-methylindoline (**9e**), and *a mixture* of 6- (**11**) and 7-methyl-6,7-dihydro-5*H*-1-pyrindine (**12**) in the ratio of 4.44 at 400 °C and 3.87 at 650 °C (not 7 as reported in ref 1). The identity of the compounds in this mixture was established by comparison with authentic samples and their ratio by measurement of the relative areas of the methyl doublet in the NMR spectrum. An authentic sample of 6-methyl-6,7-dihydro-5*H*-1-pyrindine (**11**) was prepared (together with the 5-methyl isomer from which it was separated by fractional crystallization of the picrates) from the octahydro derivatives by a modification of the method of Lochte and Pittman.[19] Authentic 7-methyl-6,7-dihydro-5*H*-1-pyrindine (**12**) was synthesized by methylation of the active methylene in **7a** with lithium diisopropylamide and then methyl iodide. From these flash vacuum pyrolyses it is clear that the C_β position in **1** becomes mainly C_6 in **7**, though some "scrambling" occurs and C_β appears to a certain extent as C_7 in **7**.

When 1-phenyl-2-propanesulfonyl azide (**1f**) was pyrolyzed at 650 °C, β-methylstyrene (1.4%) and 3-methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**2f**) (8.4%) were formed, together with a mixture of **11** and **12** (17.3%) in the molar ratio of 4.3. Thus, *this ratio is the same*, within experimental error, *as that of* ***11*****:****12** *obtained from* ***1e*** *at 650 °C*. On the other hand, FVP of **1f** at



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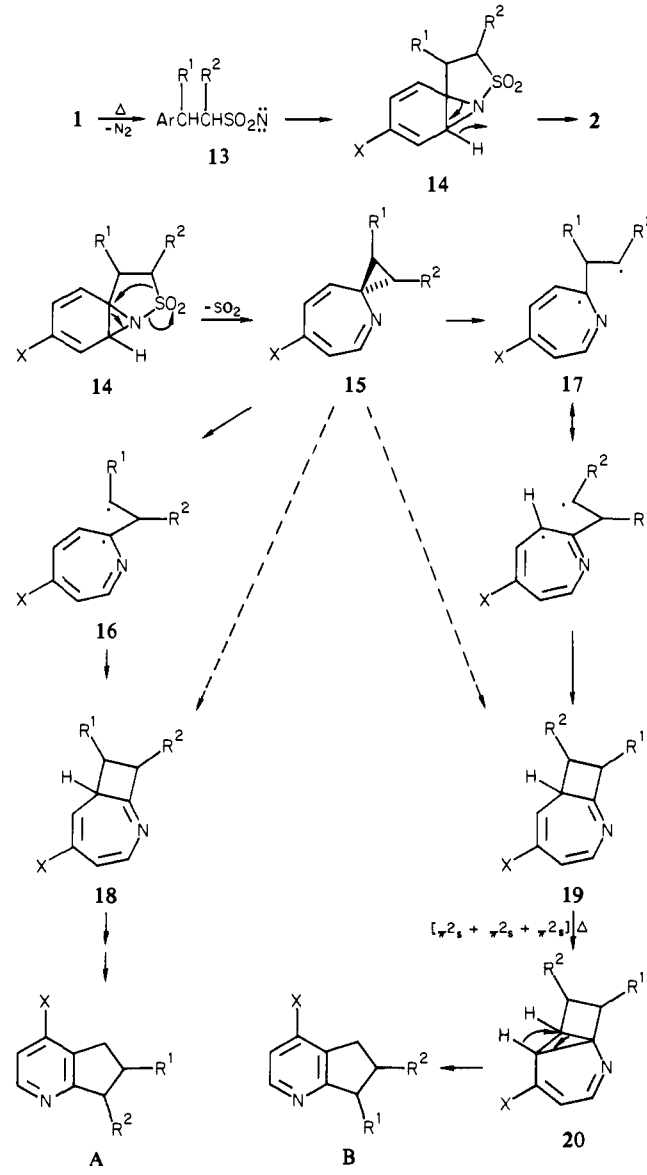
400 °C gave a mixture of **11** and **12** (10.9%) in the ratio of 5.8, together with β-methylstyrene (1.4%) and **2f** (14%). We assume that a much greater experimental error existed in the measurement of the ratio **11**:**12** for this 400 °C reaction since the actual yield of **12** was only 1.6% and the area of the corresponding methyl doublet was subject to larger uncertainty.

It should be noted in passing that the C_2–H proton in some compounds **7** gave rise to a broad unresolved peak in the NMR spectrum determined in $CDCl_3$ solution (undoubtedly resulting from quadrupole broadening by the adjacent nitrogen atom) but that the normal expected resolution could be restored by the addition of one drop of trifluoroacetic acid to the deuteriochloroform solution. It is also important to point out that the dihydropyrindines did not rearrange under the FVP conditions, though the decreased yield of **7d** at 650 °C compared to that at 400 °C suggests that this compound (or an intermediate leading to it) may be thermally unstable.

Thus, both **1e** and **1f** give **11** and **12** in almost the same ratio at 650 °C. One is, therefore, forced to the likely conclusion that

Scheme I



11 and **12** must derive from a common intermediate formed from both **1e** and **1f**. Many mechanisms can be written to accommodate all the above facts, and the simplest is given in Scheme I. The first step is the formation of the sulfonylnitrene (**13**) with loss of nitrogen, followed by addition[4] to the adjacent benzene ring to give a benzaziridine ring (**14**).[20] In solution, or at the lower temperatures in FVP, this will ring open as usual to the dihydrobenzothiazine **2**. Under flash vacuum pyrolytic conditions one can visualize **14** having a number of options in addition to going to **2** (if the latter goes via a dipolar intermediate, its formation will be less likely in the gas phase). In the simplest alternative, **14** eliminates SO_2 with concommitent ring expansion to give **15**. While this is written as a concerted process, it could

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(18) Abramovitch, R. A.; Wake, S. *J. Chem. Soc., Chem. Commun.* **1977**, 673.
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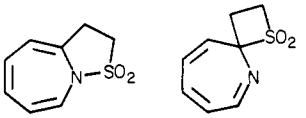
(20) By analogy with the intramolecular 1,2-shift in an arylnitrene—generated at 8 K in an argon matrix—to give a didehydroazepine without going through a benzazirine,[21] one could postulate a direct insertion of a sulfonylnitrene into a benzene σ bond to give an *N*-sulfonylazepine directly without going to an aziridine intermediate. This seems energetically unlikely in comparison with an intermolecular (or its intramolecular equivalent with **21**) attack of the electron-deficient nitrene on the π system. Even in the intramolecular case, evidence for a naphthazirine precursor to the dehydroazepine has been found recently.[22]
(21) Chapman, O. L.; LeRoux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282. Chapman, O. L.; Sheridan, R. S.; LeRoux, J. P. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 334.
(22) Dunkin, I. R.; Thomson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1980**, 499.

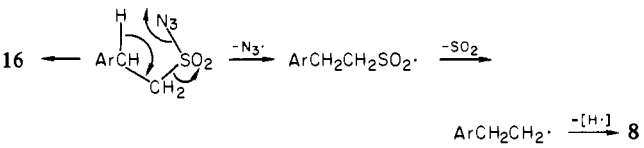
well be a stepwise one involving diradical intermediates. An alternative would be an electrocyclic expansion to **21** and thence to **15** or going through **22**. Clearly, further work is required before



21 **22**

any details are filled in. The spiroazepinocyclopropane **15** could then rearrange to a mixture of cyclobutane derivatives **18** and **19**, probably via a diradical process as shown. The allowed concerted thermal 1,7-shift requires an inversion at the migration center, and this seems sterically prohibited in this 1-methylspiro[2.6]-azanona-4,6,8-triene system. Thus, for inversion to occur at the migrating center the latter would have to swing out and away from the ring and hence from the π system. A stepwise diradical mechanism has been postulated to explain a similar rearrangement observed with 1-phenylspiro[2.6]nona-4,6,8-triene[23] and for a related process.[24] At the relatively high temperatures employed a "forbidden" 1,7-suprafacial concerted process[25] cannot be excluded, however. The final steps would now be straightforward: electrocyclic ring closure, e.g., to **20** followed by expansion of the four- to a five-membered ring with hydrogen migration as shown would give the dihydropyrindines A and B. The scheme is also in accord with the fact that the ratio of A to B is the same at 650 °C irrespective of whether **2e** or **2f** is used, since **15** (R^1 = Me, R^2 = H) is the same as **15** (R^1 = H, R^2 = Me). In the case in which R^1 = Me and R^2 = H, homolysis of **15** to give **16** would be expected to be favored (secondary radical more stable than primary one), and this would result in more A (R^1 = Me, R^2 = H) being formed than B (and vice versa when R^2 = Me and R^1 = H). Modifications may eventually have to be made to the scheme in light of further experiments which are being continued.

Styrene formation probably initially involves loss of an azide radical. This was shown to occur in the decomposition of mesitylenesulfonyl azide in *n*-dodecane when dodecyl azides were isolated from among the products.[11a] Kinetic data have also pointed to their formation.[13] This would then be followed by loss of SO_2 to give β-phenethyl radical from which hydrogen abstraction would lead to the styrene. Alternatively, a cyclic concerted process may be visualized.



Experimental Section

Melting points are uncorrected. IR spectra were determined on Perkin-Elmer 257, 357, or Beckman Acculab 3 instruments and NMR spectra on a Varian Associates HA-100 or a Hitachi Perkin-Elmer R20B spectrometer using tetramethylsilane as internal standard. The mass spectra were determined on a CEC 21-104 or Hitachi Perkin-Elmer RMU-6M spectrometer and UV spectra on a Cary 14 spectrophotometer. Gas chromatographic analyses were carried out on a Varian-Aerograph 1700 gas chromatograph using helium as a carrier gas.

Reagents and solvents were usually reagent grade and were fractionally distilled or recrystallized before use. Drying of organic extracts was effected with calcium chloride, magnesium sulfate, or molecular sieves (Davidson, Type 4A, grade 514, 8–12 mesh). Petroleum ether refers to the fraction bp 30–60 °C unless otherwise stated. Basic alumina for column chromatography was Alcoa (F-20) and neutral alumina was prepared by taking this basic alumina, boiling it with distilled water, neutralizing with acetic acid, rinsing with a large volume of distilled water, and activated by heating at 375 °C for 12 h, followed by cooling it in a vacuum desiccator. Dry, oxygen-free, nitrogen was obtained by passing commercial grade nitrogen through a train consisting of a basic solution of pyrogallol, then sulfuric acid, and finally anhydrous calcium chloride. Calculations of the yields are based on unrecovered starting material.

β-Phenethylsulfonyl Azide. A solution of β-phenethylsulfonyl chloride[26] (18.7 g, 0.092 mol) in acetone (200 mL) was cooled to 5 °C in an ice bath, and then a solution of sodium azide (6.5 g, 0.10 mol) in water (50 mL) was added dropwise with stirring. A further 30 mL of water was added, and the solution was stirred at room temperature for 12 h, concentrated in vacuo behind a safety shield to about 75 mL, and poured into water (300 mL). The colorless oil which separated was extracted with ether (3 × 100 mL), and the ether layer washed with water (100 mL), 5% aqueous Na_2CO_3 (100 mL), and water (2 × 100 mL) and dried ($CaCl_2$). The solvent was evaporated, and the residual oil was distilled (safety shield) to give β-phenethylsulfonyl azide (13.9 g, 72%): bp 92 °C (35 μm); IR (film) 2140 (s), 1370 (s), 1200 cm^{-1} (s, br); NMR (CCl_4) δ 7.14 (m, 5 H, ArH), 3.40 (m, 2 H, C_αH), 3.08 (m, 2 H, C_βH); mass spectrum (70 eV), *m/e* (relative intensity) 119 ($M^{+\cdot} - SO_2 - N_2$) (66), 118 (96), 117 (22), 105 (12), 104 (100), 103 (45), 91 (34), 78 (40), 77 (25), 69 (12), 66 (11), 65 (22), 63 (19), 52 (12), 51 (30), 50 (14). Anal. Calcd for $C_8H_9N_3O_2S$: C, 45.49; H, 4.29. Found: C, 45.65; H, 4.36.

Thermolysis of β-Phenethylsulfonyl Azide. (a) In Cyclohexane. The azide (1.321 g) in cyclohexane (18 mL, Na dried and flushed with dry, O_2-free N_2) was thermolyzed in a glass-lined steel bomb with stirring[27] at 135 °C for 36 h. After being cooled, the bomb was opened and a strong smell of SO_2 was present. The solution was clear and contained a number of white needles together with some black gummy solid. The products from two such runs were combined, the vessels being washed with ethyl acetate (2 × 20 mL), and evaporated in vacuo onto neutral alumina (10 g). The products were then chromatographed on a column of neutral alumina (2.3 × 25 cm) prepared in petroleum ether. Elution with C_6H_6–ethyl acetate (85:15, v/v) gave *N*-cyclohexyl-β-phenethylsulfonamide (1.33 g, 50%), identical (IR, NMR, mp) with an authentic sample prepared as described below. Elution with C_6H_6–ethyl acetate (1:1, v/v) gave a tan solid which was sublimed at 130 °C (5 μm) to give 3,4-dihydro-2,1-benzothiazine 2,2-dioxide (0.163 g, 7.1%): mp 156–157 °C (lit.[8] 154–155 °C); IR (KBr) 3230 (s, br), 1315 (s), 1160 (s), 1130 cm^{-1} (s); NMR ($CDCl_3$) δ 7.41–7.05 (m, 3 H), 6.90–6.65 (m, 2 H, reduces to 1 H (m) at δ 6.84 on shaking with D_2O), 3.41 (m, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 185 (2), 184 (4), 183 ($M^{+\cdot}$, 34), 119 (23), 118 (100), 117 (13), 91 (26). Elution with ethyl acetate–ethanol (98:2, v/v) gave β-phenethylsulfonamide (0.151 g, 6.5%): mp 123–124 °C (lit.[1] 119 °C) after sublimation at 135 °C (5 μm), identical with an authentic sample.[26]

(b) In Benzene. The azide (2.646 g) in dry benzene (70 mL) was flushed with oxygen-free N_2 and heated at 135 °C for 36 h. The smell of SO_2 was obvious when the bomb was opened. Chromatography as under a above and elution with benzene–ethyl acetate (98:2, v/v) gave a tan-yellow oil (0.457 g) which darkened on standing. Rechromatography under the same conditions gave a yellow oil (0.291 g) which solidified on standing in the dark. Recrystallization from petroleum ether (bp 30–60 °C) at −78 °C in the absence of light gave *N*-(β-phenethylsulfonyl)azepine (0.139 g, 4.2%) as yellow plates: mp 35–36 °C; IR (KBr) 1350 (s), 1155 (s), 740 (s), 705 cm^{-1} (m); NMR ($CDCl_3$) δ 7.3–7.1 (m, 5 H, ArH), 6.21 (m, 2 H, C_2–H and C_7–H of azepine), 5.77 (m, 4 H, C_3–H, C_5–H, C_6H of azepine), 3.17 (complex symmetrical multiplet, 4 H, C_α–H, C_β–H); mass spectrum (70 eV), *m/e* (relative intensity) 261 ($M^{+\cdot}$, 2), 105 (18), 93 (13), 92 (100), 77 (11), 65 (43). The compound appeared to be very sensitive to light and satisfactory microanalytical data could not be obtained. Anal. Calcd for $C_{14}H_{16}NO_2S$: C, 64.34; H, 5.78. Found: C, 63.02; H, 5.68.

Elution with benzene–ethyl acetate (95:5, v/v) gave a series of fractions, the first part of which were light tan crystals mixed with an oil, and the latter were only oily. Since the tan crystals were slightly soluble in acetone, it was added to those fractions containing crystalline material; the crystals were filtered and dried. Concentration of the acetone solution gave a second crop of white crystals (total yield = 0.093 g) which are tentatively identified as a dimer of *N*-(β-phenethylsulfonyl)azepine (2.8%): mp 283–284 °C (dec); IR (KBr) 1335 (s), 1150 cm^{-1} (s); NMR ($CDCl_3$) δ 7.3–7.1 (br m), 6.4 (m), 6.3 (m), 6.0 (m), 5.95 (m), 4.44 (m), 3.4–3.0 (m); no satisfactory integration could be obtained; mass spectrum (70 eV) was identical with that of *N*-phenyl-β-phenethylsulfonamide (vide infra). Anal. Calcd for $(C_{14}H_{15}NO_2S)_2$: C, 64.34; H, 5.78. Found: C, 64.40; H, 5.90.

Elution with benzene–ethyl acetate (85:15, v/v) gave a tan oil which solidified on standing (0.189 g, 5.8%) and was identical (IR, NMR, MS) with an authentic sample of *N*-phenyl-β-phenethylsulfonamide. Elution with ethyl acetate gave 3,4-dihydro-2,1-benzothiazine 2,2-dioxide (0.149

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(27) Abramovitch, R. A.; Williams, J. S. *Chem. Ind. (London)* **1965**, 1786.

g, 6.5%). Elution with ethyl acetate–ethanol (98:2 and 95:5, v/v) gave β-phenethylsulfonamide (0.161 g, 6.8%).

(c) In Diglyme. The azide (1.567 g) in diglyme (60 mL) was heated with stirring at 149 °C for 19 h to give SO_2 (10%) (collected in KOH solution and estimated as $BaSO_4$), 3,4-dihydro-2,1-benzothiazine 2,2-dioxide (0.082 g, 6%), and β-phenethylsulfonamide (0.420 g, 30.6%).

(d) In Freon 113. The azide (2.682 g) in Freon 113 (60 mL) was heated at 135 °C for 36 h. Chromatography as above yielded 3,4-dihydro-2,1-benzothiazine 2,2-dioxide (0.660 g, 28%) and β-phenethylsulfonamide (0.288 g, 12%).

***N*-Cyclohexyl-β-phenethylsulfonamide.** To a solution of β-phenethylsulfonyl chloride (1.05 g) in dry ether (150 mL) was added cyclohexylamine (5 mL) dropwise with stirring at room temperature. After 2 h, the solution was filtered through Celite, the Celite was washed with ether (2 × 20 mL), and the combined filtrates were extracted with 2 N HCl (2 × 50 mL). The ether layer was treated with charcoal, dried ($CaCl_2$), and evaporated to give the amide (1.07 g, 80%): mp 80 °C (from petroleum ether); IR (KBr) 3260 (m), 1310 (s), 1145 cm^{-1} (s); NMR ($CDCl_3$) δ 7.31 (s, 5 H, ArH), 4.27 (d, J = 8 Hz, 1 H, exchangeable with D_2O, NH), 3.4–3.0 (complex m, 4 H, C_α–H, C_β–H), 2.1–1.0 (m, 11 H, C_6H_{11}); mass spectrum (70 eV), *m/e* (relative intensity) 224 (11), 105 (82), 104 (100), 99 (14), 98 (17), 79 (12), 77 (16), 57 (11), 56 (22), 55 (13), 43 (13), 41 (15); no $M^{+\cdot}$ peak at *m/e* 267. Anal. Calcd for $C_{14}H_{21}NO_2S$: C, 62.89; H, 7.92. Found: C, 62.77; H, 8.01.

***N*-Phenyl-β-phenethylsulfonamide.** This was prepared in the same way as the *N*-cyclohexyl derivative above from the sulfonyl chloride (1.55 g) and aniline (5 mL) to give the amide (1.21 g, 61%): mp 75–76 °C (from aqueous EtOH) (lit.[26] mp 77 °C).

Sodium 4-Methyl-β-phenethylsulfonate. 4-Methyl-β-phenethyl bromide[28] (51.0 g) was added to an aqueous solution (600 mL) of anhydrous sodium sulfite (56.3 g) and boiled under reflux with stirring for 18 h. The suspension was filtered from a small amount of white insoluble material (<100 mg, probably polymer) and cooled to 0 °C. The white plates which separated were collected, pressed dry, and then dried under vacuum at 60 °C to give the sodium salt (50.8 g, 89%): mp >320 °C; IR (KBr) 3450 (m, br), 1255 (s), 1220 (s), 1185 (s), 1075 (s), 1060 (s), 805 cm^{-1} (s). Anal. Calcd for $C_9H_{11}NaO_3S$: C, 48.64; H, 4.99. Found: C, 48.53; H, 5.03.

4-Methyl-β-phenethylsulfonyl Chloride. A solution of the sodium sulfonate (49.5 g) in dry benzene (400 mL) was treated with dimethylformamide (1.0 g), and then $SOCl_2$ (33.5 g) was added dropwise. The solution was boiled under reflux for 4 h, cooled, and filtered through Celite, the Celite washed with dry benzene (40 mL), and the solvent evaporated to give a low melting solid. Recrystallization from petroleum ether at −78 °C gave the sulfonyl chloride (36.2 g, 75%): mp 66–66.5 °C; mass spectrum (70 eV), *m/e* (relative intensity) 220 ($M^{+\cdot}$, ^{37}Cl, 2), 218 ($M^{+\cdot}$, ^{35}Cl, 6) 119 (52), 118 (100), 117 (25), 105 (21), 91 (29), 77 (12), 65 (18), 51 (11), 41 (16), 39 (20). Anal. Calcd for $C_9H_{11}ClO_2S$: C, 49.43; H, 5.07. Found: C, 49.26; H, 5.16.

4-Methyl-β-phenethylsulfonyl Azide. This was prepared as in the case of the phenethyl compound except that the crude product was extracted with ethyl acetate. The crude solid azide was recrystallized from petroleum ether at −78 °C to give pure product (79%): mp 63.5–64.5 °C; IR (KBr) 2130 (s), 1350 (s), 1200 (s), 1145 (s), 750 (s), 740 cm^{-1} (s); NMR ($CDCl_3$) δ 7.11 (s, 4 H), 3.32 (m, 4 H), 2.28 (s, 3 H); mass spectrum (70 eV), *m/e* (relative intensity) 225 ($M^{+\cdot}$, 22) 119 (100), 118 (99), 105 (25), 91 (60), 77 (23), 65 (22). Anal. Calcd for $C_9H_{11}N_3O_2S$: C, 47.99; H, 4.92. Found: C, 48.03; H, 4.90.

Thermolysis of 4-Methyl-β-phenethylsulfonyl Azide. The azide (6.232 g) was added to Freon 113 (195 mL) and the solution flushed with dry, oxygen-free nitrogen and then heated in glass lined steel bombs with stirring at 135 °C for 36 h. The solution was combined with the ethyl acetate washings of the reaction vessels and evaporated onto neutral alumina (15 g) in vacuo. The products were then chromatographed on a column of neutral alumina (2.3 × 25 cm) prepared in benzene. Elution with benzene–ethyl acetate (1:2, v/v) gave a tan solid which was sublimed (125 °C (5 μm)) to give 7-methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (2.08 g, 38.1%) as a white solid: mp 157–158 °C; IR (KBr) 3280 (s), 1430 (s), 1325 (s), 1165 (s), 1140 cm^{-1} (s); NMR ($CDCl_3$) δ 7.04 (d, $J_{5,6}$ = 8.0 Hz, 1 H), 6.93 (d, $J_{5,6}$ = 8.0 Hz, 1 H), 6.6 (br s, 1 H, exchangeable with D_2O, NH), 6.55 (s, 1 H, H_8), 3.34 (m, 4 H), 2.27 (s, 3 H, Me); mass spectrum (70 eV), *m/e* (relative intensity) 197 ($M^{+\cdot}$, 37), 132 (100). Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62. Found: C, 54.83; H, 5.66.

Elution with ethyl acetate and ethyl acetate–ethanol (99:1, v/v) gave a solid which, on sublimation (135 °C @ 5 μ), gave 4-methyl-β-phenethylsulfonamide (0.592 g, 10%), in all respects identical with an authentic sample (see below). Elution with ethyl acetate–ethanol (85:15, v/v) gave a black tar (0.540 g) from which no pure product could be obtained.

4-Methyl-β-phenethylsulfonamide. This was prepared from the sulfonyl chloride (4.21 g) in dry ether (100 mL) and dry ammonia gas. Ammonium chloride precipitated. The suspension was filtered through Celite, the Celite washed with ether (2 × 10 mL), and the ether evaporated to give the amide (3.21 g, 84%): mp 114–115 °C [from petroleum ether (bp 60–110 °C)]; IR (KBr) 3365 (s), 3270 (s), 1320 (s), 1150 (s), 1130 cm^{-1} (s); NMR ($CDCl_3$) δ 7.10 (s, 4 H), 4.86 (s, 2 H, NH_2), 3.19 (m, 4 H), 2.27 (s, 3 H, Me); mass spectrum (70 eV), *m/e* (relative intensity) 199 ($M^{+\cdot}$, 7), 118 (100). Anal. Calcd for $C_9H_{13}NO_2S$: C, 54.24; H, 6.57. Found: C, 54.22; H, 6.65.

***N*-Cyclohexyl-4-methyl-β-phenethylsulfonamide** [mp 112–112.5 °C, from petroleum ether (bp 60–110 °C)] was prepared (88% yield) as for the phenyl compound. Anal. Calcd for $C_{15}H_{23}NO_2S$: C, 64.02; H, 8.24. Found: C, 63.98; H, 8.26.

Sodium 4-Chloro-β-phenethylsulfonate. This was prepared (81%) in the same manner as the corresponding 4-methyl compound, starting with 4-chloro-β-phenethyl bromide:[29] mp >320 °C; IR (KBr) 3450 (m, br), 1255 (s), 1220 (s), 1185 (s), 1070 cm^{-1} (s). Anal. Calcd for $C_8H_8ClNaO_3S$: C, 39.59; H, 3.32. Found: C, 39.41; H, 3.39.

4-Chloro-β-phenethylsulfonyl Chloride. The acid chloride was prepared (82%) as was the corresponding 4-methyl derivative: mp 83.5–84 °C (from petroleum ether at −78 °C); IR (KBr) 1355 (s), 1155 cm^{-1} (s); NMR ($CDCl_3$) δ 7.35 (d, $J_{2,3}$ = 9.1 Hz, 2 H), 7.14 (d, $J_{2,3}$ = 9.1 Hz, 2 H), 4.03–3.65 (m, 2 H), 3.45–3.05 (m, 2 H); mass spectrum (70 eV), *m/e* (relative intensity) 242 ($M^{+\cdot}$, 2 ^{37}Cl, 3), 240 ($M^{+\cdot}$, ^{37}Cl, ^{35}Cl, 12), 238 ($M^{+\cdot}$, 2 ^{35}Cl, 15), 138 (100). Anal. Calcd for $C_8H_8Cl_2O_2S$: C, 40.18; H, 3.37. Found: C, 40.33; H, 3.45.

4-Chloro-β-phenethylsulfonyl Azide. This was prepared in 79% yield as described above for other azides: mp 74–74.5 °C [from petroleum ether (bp 60–110 °C)]; IR (KBr) 2360 (m), 2140 (s), 1355 (s), 1195 (s), 1150 cm^{-1} (s); NMR ($CDCl_3$) δ 7.35 (d, $J_{2,3}$ = 9.0 Hz, 2 H), 7.14 (d, $J_{2,3}$ = 9.0 Hz, 2 H), 3.75–3.40 (m, 2 H), 3.30–2.95 (m, 2 H); mass spectrum (70 eV), *m/e* (relative intensity) 247 ($M^{+\cdot}$, ^{37}Cl, 0.6), 245 ($M^{+\cdot}$, ^{35}Cl, 1.6), 103 (100). Anal. Calcd for $C_8H_8ClN_3O_2S$: C, 39.11; H, 3.28. Found: C, 39.11; H, 3.33.

Thermolysis of 4-Chloro-β-phenethylsulfonyl Azide. The decomposition was carried out in Freon 113 at 135 °C for 36 h as before. Column chromatography on neutral alumina (2.3 × 25 cm) and elution with benzene–ethyl acetate (1:1, v/v) gave 7-chloro-2,4-dihydro-2,1-benzothiazine 2,2-dioxide (1.6%): mp 199–200 °C (sublimed at 120 °C (3 μm)); IR (KBr) 3270 (m), 1380 (s), 1315 (s), 1160 (s), 1135 cm^{-1} (s); NMR ($CDCl_3$) δ 7.04 (s, $J_{5,6}$ = 8.0 Hz, 1 H, H_5) 6.83 (dd, $J_{5,6}$ = 8.0 Hz, $J_{6,8}$ = 1.8 Hz, 1 H, H_6), 6.60 (br s, 1 H, exchangeable with D_2O, NH), 6.55 (d, $J_{6,8}$ = 1.8 Hz, 1 H, H_8), 3.46–3.01 (m, 4 H, H_3, H_4); mass spectrum (70 eV), *m/e* (relative intensity) 219 ($M^{+\cdot}$, ^{37}Cl, 16), 217 ($M^{+\cdot}$, ^{35}Cl, 44), 118 (100). Anal. Calcd for $C_8H_8ClNO_2S$: C, 44.14; H, 3.70. Found: C, 44.14; H, 3.71.

Elution with benzene–ethyl acetate (1:2, v/v) gave 4-chloro-β-phenethylsulfonamide (5.8%): mp 133.5–134 °C [from petroleum ether (bp 60–110 °C)], identical with an authentic sample prepared in 84% yield from the sulfonyl chloride and ammonia; IR (KBr) 3375 (m), 3230 (m), 1305 (s), 1115 cm^{-1} (s); NMR (acetone-d_6) δ 7.35 (s, 4 H, ArH), 6.23 (br s, 2 H, exchangeable NH_2) 3.28 (m, 4 H, H_α, H_β); mass spectrum (70 eV), *m/e* (relative intensity) 221 ($M^{+\cdot}$, ^{37}Cl, 2), 219 ($M^{+\cdot}$, ^{35}Cl, 5), 138 (100). Anal. Calcd for $C_8H_{10}ClNO_2S$: C, 43.74; H, 4.59. Found: C, 43.58; H, 4.60.

Sodium 4-Methoxy-β-phenethylsulfonate. Prepared in the usual manner from the bromide[30] this was obtained in 77% yield: mp >320 °C; IR (KBr) 3450 (m, br), 1250 (s), 1220 (s), 1185 cm^{-1} (s). Anal. Calcd for $C_9H_{11}NaO_4S$: C, 45.37; H, 4.65. Found: C, 45.36; H, 4.62.

4-Methoxy-β-phenethylsulfonyl Chloride. Prepared from the corresponding sodium sulfonate (55.0 g) as above it was obtained as colorless needles (36.3 g, 67%): mp 41–41.5 °C (from petroleum ether at −78 °C); IR (KBr) 1365 (s), 1255 (s), 1170 cm^{-1} (s); NMR ($CDCl_3$) δ 7.18 (d, $J_{2,3}$ = 9.1 Hz, 2 H), 6.85 (d, $J_{2,3}$ = 9.1 Hz, 2 H), 3.77 (s superimposed on a multiplet, 3 H, OCH_3), 4.1–3.6 (m, 2 H), 3.4–3.0 (m, 2 H); mass spectrum (70 eV), *m/e* (relative intensity) 236 ($M^{+\cdot}$, ^{37}Cl, 4), 234 ($M^{+\cdot}$, ^{35}Cl, 11), 134 (99), 121 (100). Anal. Calcd for $C_9H_{11}ClO_3S$: C, 46.09; H, 4.72. Found: C, 45.91; H, 4.75.

4-Methoxy-β-phenethylsulfonyl Azide. This was obtained in 58% yield from the sulfonyl chloride as usual: mp 42–43 °C (from petroleum ether at −78 °C). IR (KBr) 2350 (m), 2140 (s), 1340 (s), 1245 (s), 1150 cm^{-1}

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(s); NMR ($CDCl_3$) δ 7.13 (d, $J_{2,3}$ = 9.0 Hz, 2 H), 6.83 (d, $J_{2,3}$ = 9.0 Hz, 2 H), 3.74 (s, 3 H, OCH_3), 3.8–3.35 (m, 2 H), 3.35–2.90 (m, 2 H): mass spectrum (70 eV), *m/e* (relative intensity) 241 ($M^{+\cdot}$, 1.5), 91 (100). Anal. Calcd for $C_9H_{11}N_3O_3S$: C, 44.80; H, 4.60. Found: C, 44.60; H, 4.56.

Thermolysis of 4-Methoxy-β-phenethylsulfonyl Azide. Decomposition in Freon 113 under dry, O_2-free N_2 for 36 h at 135 °C gave a mixture which was resolved as usual on neutral alumina to give:

7-Methoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (39%): mp 148–149 °C [from ethyl acetate–petroleum ether (bp 60–110 °C)]; IR (KBr) 3190 (m), 1310 (s), 1240 (s), 1160 (s), 1130 cm^{-1} (s); NMR ($CDCl_3$) δ 8.05 (br s, 1 H, exchangeable, NH), 6.87–6.66 (m, 3 H, ArH), 3.74 (s, 3 H, OCH_3), 3.45–3.10 (m, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 213 ($M^{+\cdot}$, 40), 134 (100). Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20. Found: C, 50.69; H, 5.25.

4-Methoxy-β-phenethylsulfonamide (15.7%): mp 119.5–120 °C [from petroleum ether (bp 60–110 °C)], identical with an authentic sample prepared from the sulfonyl chloride and dry ammonia (86% yield); IR (KBr) 3345 (s), 3250 (s), 1300 (s), 1235 (s), 1150 cm^{-1} (s); NMR ($CDCl_3$–acetone-d_6, 1:1 v/v) δ 7.15 (d, $J_{2,3}$ = 8.8 Hz, 2 H), 6.80 (d, $J_{2,3}$ = 8.8 Hz, 2 H), 5.74 (br s, 2 H, exchangeable, NH_2), 3.72 (s, 3 H, OCH_3), 3.15 (m, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 215 ($M^{+\cdot}$, 16), 134 (100). Anal. Calcd for $C_9H_{13}NO_3S$: C, 50.21; H, 6.09. Found: C, 50.22; H, 6.03.

2-Phenylpropanesulfonyl Azide. This was prepared from the corresponding sulfonyl chloride (22.3 g) as a light yellow oil which was extracted with benzene (2 × 200 mL); the organic layer was washed with water (100 mL), 5% aqueous Na_2CO_3 (2 × 100 mL), and then again with water (100 mL) and dried ($CaCl_2$). Evaporation of the solvent gave an oil which crystallized from petroleum ether at −78 °C. The crystals, free of solvent, were brought to room temperature under high vacuum to give the pure azide (16.7 g, 72%) as a colorless oil; IR (film) 2370 (w), 2140 (s), 1370 (s), 1200 (s), 1160 cm^{-1} (s); NMR ($CDCl_3$) δ 7.27 (m, 5 H, ArH), 3.75–3.35 (m, 3 H), 1.46 (d, J = 6.5 Hz, 3 H, CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 133 ($M^{+\cdot} - SO_2 - N_2$, 12), 132 (13), 119 (20), 118 (71), 117 (26), 115 (13), 105 (19), 104 (20), 103 (23), 91 (100), 78 (27), 77 (39), 65 (27), 64 (16), 52 (18), 51 (49), 50 (49), 50 (24), 49 (27), 41 (34), 39 (55); no $M^{+\cdot}$ peak observed. Anal. Calcd for $C_9H_{11}N_3O_2S$: C, 47.99; H, 4.92. Found: C, 47.80; H, 4.76.

Thermolysis of 2-Phenylpropanesulfonyl Azide. The azide (6.169 g) was decomposed as usual in Freon 113 (180 mL) at 135 °C for 36 h. SO_2 was detected. The mixture of products was resolved on a column (2.3 × 25 cm) of neutral alumina to give the following.

4-Methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (0.592 g, 10.9%): mp 122–123 °C (sublimation at 120 °C (5 μm)); IR (KBr) 3230 (m), 1310 (s), 1140 cm^{-1} (s); NMR ($CDCl_3$) δ 7.4–7.0 (m, 3 H, ArH), 6.9–6.6 (m, 2 H, reduces to 1 H multiplet at 6.8 upon shaking with D_2O, NH, ArH), 3.6–3.0 (m, 3 H, H_3, H_4), 1.58 (d, J_{H_4,CH_3} = 7.4 Hz, 3 H, CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 197 ($M^{+\cdot}$, 60), 132 (100), 118 (69). Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62. Found: C, 54.90; H, 5.65.

2-Phenylpropanesulfonamide (1.037 g, 19.4%): mp 72–72.5 °C (water), identical with an authentic sample prepared (64% yield) from the sulfonyl chloride and dry ammonia in dry ether; IR (KBr) 3310 (m), 3240 cm^{-1} (m); mass spectrum (70 eV), *m/e* (relative intensity) 199 ($M^{+\cdot}$, 2), 118 (100). Anal. Calcd for $C_9H_{13}NO_2S$: C, 54.25; H, 6.78. Found: C, 54.25; H, 6.81.

Sodium 1-Phenyl-2-propanesulfonate. 1-Phenyl-2-bromopropane (20 g) in ethanol (100 mL) was added to sodium sulfite (16 g, anhydrous) in water (150 mL). The mixture was stirred and boiled under reflux for 35 h, concentrated to about 30 mL, and cooled in ice. The white crystals which precipitated were filtered, washed with cold ethanol (3 × 10 mL), and dried to give the sodium sulfonate (12 g, 54%): mp >310 °C (from 35% aqueous ethanol); NMR (D_2O) δ 7.21 (s, 5 H, ArH), 3.40–2.46 (m, 3 H), 1.07 (s, J = 7 Hz, 3 H, CH_3). Anal. Calcd for $C_9H_{11}NaO_3S$: C, 48.65; H, 4.95. Found: C, 48.77; H, 4.96.

1-Phenyl-3-propanesulfonyl Chloride. Prepared as usual from the sodium sulfonate it was obtained as a pale yellow oil (8.6 g, 72.9%): bp 81–83 °C (0.01 mmHg); NMR ($CDCl_3$) δ 7.45–7.00 (m, 5 H, ArH); 4.07–3.50 (m, 2 H, H_β), 2.99–2.57 (m, 1 H, H_α), 1.47 (d, J = 7 Hz, 3 H, CH_3). Anal. Calcd for $C_9H_{11}ClO_2S$: C, 49.44; H, 5.04. Found: C, 49.37; H, 5.02.

1-Phenyl-2-propanesulfonyl Azide. This was prepared as usual from the chloride and obtained as a colorless oil (55%): bp 90–93 °C (0.01 mm); IR (film) 2350 (m), 2130 (s), 1350 (s), 1190 (s), 1155 cm^{-1} (s); NMR ($CDCl_3$) δ 7.47–7.03 (m, 5 H, ArH), 3.85–3.27 (m, 2 H, H_β), 2.93–2.50 (m, 1 H, H_α), 1.38 (d, J = 7 Hz, CH_3). Anal. Calcd for $C_9H_{11}N_3O_2S$: C, 48.00; H, 4.89. Found: C, 47.98; H, 4.93.

Thermolysis of 1-Phenyl-2-propanesulfonyl Azide. The azide (2.00 g) was decomposed in degassed (three freeze–dry–thaw cycles) Freon 113 at 135 °C for 40 h. Workup as usual gave the following: the starting azide (0.409 g, 20.5%); 3-methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (341 mg, 24.5% based on azide consumed) [mp 131–132 °C (benzene); NMR δ 7.33–6.97 (m, 3 H, H_5, H_6, H_7), 6.97 (s, 1 H, exchangeable, NH), 6.71 (dd, $J_{7,8}$ = 8.0 Hz, $J_{6,8}$ = 2.0 Hz, 1 H, H_8), 3.57–3.03 (m, 3 H, H_3, H_4), 1.45 (d, J = 6.5 Hz, 3 H, CH_3). Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.82; H, 5.58. Found: C, 54.74; H, 5.60]; 1-phenyl-2-propanesulfonamide (0.266 g, 18.9%) [mp 94.5–95 °C (benzene) NMR ($CDCl_3$) δ 7.43–7.00 (m, 5 H, ArH), 4.97 (br s, 2 H, exchangeable, NH_2), 3.00–3.03 (m, 2 H), 2.85–2.42 (m, 1 H), 1.29 (d, J = 6.5 Hz, 3 H, CH_3). Anal. Calcd for $C_9H_{13}NO_2S$: C, 54.27; H, 6.53. Found: C, 54.20, H, 6.59].

Flash Vacuum Pyrolysis. General Data. The equipment used was very simple and consisted essentially of an inlet system in a preheater, a quartz pyrolysis tube, a post-emergence heater, a cold trap, and a high capacity vacuum pump. The pyrolysis tube was 40 cm long and 2.4-cm i.d., wrapped with Chromel A heating wire and surrounded by tightly packed asbestos. The voltage requirement to maintain the appropriate column temperature in the evacuated column was determined before each run by using an iron–constantan thermocouple in the event that any oxidation of the heating wire might have increased its resistance. The inlet system varied according to whether the azide was a solid or a liquid and whether a static system or flow system was used. If the azide were solid the inlet system consisted of a modified flask connected to the pyrolysis column and enclosed in a preheater chamber. Thus, the azide was warmed *to below its decomposition temperature* under vacuum so that it vaporized (or sublimed) into the pyrolysis chamber (static system). In the flow system the azide vapors were carried into the pyrolysis tube by a flow of dry, oxygen-free nitrogen gas, the flow being controlled by passing the gas first through a capillary column and then with a Teflon needle valve. When a nitrogen flow system was used, the exit port of the inlet system was loosely plugged with glass wool to prevent solid from blowing into the pyrolysis chamber. Alternatively, the solid sample rested on a coarse sintered disk and the nitrogen was introduced through the disk from below while the whole inlet was heated in the preheater, producing a "fluidized bed" of azide from which sublimation or evaporation took place more readily. With a static system, inlet pressures of (0.1–0.3) × 10^{-3} mmHg could be achieved routinely while inlet pressures of 1.5–4.0 mmHg were observed by using the flow system. When the azide was a liquid (or a low melting solid), it could be introduced into the inlet very slowly by means of a separatory funnel (capillary tip) which could, itself, be in the preheater. The trap was usually cooled with $CHCl_3$–C_2HCl_3 (1:1, v/v) and solid CO_2 or with dry ice–acetone or, in very difficult cases, with liquid nitrogen. Two liquid nitrogen traps were interposed between the cold finger and the vacuum pump. The cold finger could be modified to permit codeposition of trapping agents with reaction condensates, or these could be frozen onto the cold finger before the beginning of the decomposition. The pyrolysis column was brought to equilibrium temperature for 30–60 min before the azide was introduced.

Flash Vacuum Pyrolysis of β-Phenethylsulfonyl Azide. Static System. (a) At 250 °C. The azide (2.695 g) was pyrolyzed by using an inlet temperature of 115 °C, a column temperature of 250 °C, an initial pressure of 8 μm (the pressure during the pyrolysis rose to 110–130 μm) and a contact time of 0.28 s. The pyrolysis took a total of 270 min. The cold finger was warmed to room temperature and washed with acetone (2 × 75 mL), the acetone solution was evaporated onto neutral alumina (10 g) and placed on top of a column of neutral alumina (2.3 × 25 cm) prepared in petroleum ether. The first liquid-nitrogen trap evolved SO_2 upon warming. The pyrolysis tube showed very little carbonization, and the inlet contained only a small amount (ca. 10 mg) of dark insoluble residue. Elution of the column with benzene–petroleum ether (1:1, v/v) and with benzene gave starting azide (0.941 g, 35%). Elution with benzene–ethyl acetate (1:1, v/v) and then ethyl acetate gave 3,4-dihydro-2,1-benzothiazine 2,2-dioxide (0.85 g, 5.6%). Elution with ethyl acetate–ethanol (98:2, v/v) gave β-phenethylsulfonamide (0.091 g, 6.0%).

(b) At 300 °C. The azide (2.748 g) was pyrolyzed as above except that the column temperature was 300 °C. The pressure during the pyrolysis rose to 330–340 μm. The contact time was 0.45 s. Elution of the alumina column with benzene–ethyl acetate (95:5, v/v) gave an oil which was purified by gas chromatography [column, OV-17 (10%) on Gas Chrom Q, 6 ft × $^3/_{16}$ in., column temperature 150 °C, the flow rate 50 mL/min] to give 6,7-dihydro-5*H*-1-pyrindine (0.108 g, 6.9%): IR spectrum identical with that in the literature;[31] NMR ($CDCl_3$) δ 8.16 (d, $J_{2,3}$ = 5.4 Hz, 1 H, H_2), 7.34 (d, $J_{3,4}$ = 6.8 Hz, 1 H, H_4), 6.86 (dd, $J_{2,3}$ = 5.4 Hz, $J_{3,4}$ = 6.8 Hz, 1 H, H_3), 2.89 (m, 4 H, H_5, H_7), 2.05 (m, 2 H, H_6); mass spectrum (70 eV), *m/e* (relative intensity) 119 ($M^{+\cdot}$, 63), 118 (100). Anal. Calcd for C_8H_9N: C, 80.63; H, 7.61. Found: C, 80.53; H, 7.64. Picrate: mp 181–182 °C (lit.[32] 181–182 °C).

(31) Godar, E. M.; Mariella, R. P. *Appl. Spectrosc.* **1961**, *15*, 29.

Elution with ethyl acetate gave 3,4-dihydro-2,1-benzothiazine 2,2-dioxide (0.303 g, 12.8%). Elution with ethyl acetate–ethanol (85:15, v/v) gave a tan solid (0.129 g) whose IR spectrum was similar to that of the above benzothiazine but which could not be sublimed. It was not studied further at this time.

(c) At 350 and 400 °C. The results are summarized in Table I.

Flow System. (a) At 400 °C. The azide (0.6800 g) was pyrolyzed at 400 °C with an inlet temperature of 125 °C over a period of 65 min. The initial pressure was 3.70mmHg and rose to ca. 3.80mmHg during the pyrolysis with a nitrogen flow of 31 mL/min at 760mmHg. The contact time was 0.36 s. SO_2 was detected in the liquid N_2 trap. The pyrolysis products were washed off the dry ice trap with ethyl acetate (50 mL), and the trap was rinsed with ethyl acetate (2 × 20 mL). *o*-Dichlorobenzene (0.1296 g) (internal standard) was added to the combined washings, and the solution was concentrated down to ca. 5 mL by distillation through a 30-cm Vigreux column. The products were analyzed by gas chromatography on an 8 ft × $^3/_{16}$ in. column of 10% OV-17 on Gas Chrom Q by using an inlet temperature of 330 °C, a detector temperature of 350 °C, the column being temperature programmed after a 100-s isothermal hold at 150–310 °C at 20 °C/min, and the flow rate of 100 mL/min. The peak with retention time of 70 s was collected and identified as styrene by comparison of its IR, NMR, and mass spectra with those of an authentic sample. The peak with a retention time of 251 s was similarly identified as 6,7-dihydro-5*H*-1-pyrindine, and the peak with a retention time of 758 s was also collected and similarly identified as 3,4-dihydro-2,1-benzothiazine 2,2-dioxide. The quantitative results are summarized in Table I.

(b) At 650 °C. The azide (0.6801 g) was pyrolyzed as above except that the column temperature was 650 °C, the contact time was 0.25 s, and the pyrolysis took 60 min. In addition to the above products (cf. 450 °C) indoline (retention time = 348 s) and indole (420 s) were collected from the gas chromatographic separation and characterized by comparison with authentic samples. The quantitative results are summarized in Table I.

(c) At 300 °C Using a Nitrogen–Toluene Carrier Gas Flow. The flow system was modified by the addition of a 250-mL three-necked round-bottom flask fitted with inlet and exit tubes and a stopper and connected to the apparatus just after the nitrogen inlet stopcock. The flask was charged with toluene (ca. 50 ml) and cooled to −50 °C in a $CHCl_3$–solid CO_2 bath and the nitrogen gas stopcock opened. The temperature of −50 °C was found to result in the condensation of a uniform film of toluene on the cold finger. The pyrolysis was then carried out as before by using an inlet temperature of 120 °C, a column temperature of 300 °C, and a pressure of 0.33mmHg during the pyrolysis. The results are summarized in Table I. No bibenzyl was detected.

(d) At 350 °C with Co-condensation of Ammonia. The azide (4.655 g) was pyrolyzed by using a nitrogen flow (31 mL/min) except that dry ammonia was codeposited onto the cold finger during the pyrolysis. The only products which could be isolated and identified were dihydropyrindine (0.217 g, 8.3%) and dihydrobenzothiazine dioxide (0.233 g, 5.8%). A number of other very minor products were detected by TLC but could not be characterized.

Similar results were obtained by using an aniline film.

Flash Vacuum Pyrolysis of 3,4-Dihydro-2,1-benzothiazine 2,2-Dioxide. The sultam (0.1865 g) was pyrolyzed at 650 °C by using an inlet temperature of 130 °C and a nitrogen flow rate of 31 mL/min. It took 2.5 h to complete the pyrolysis and the contact time was 0.27 s. Analysis of the products by gas chromatography as above showed the formation of indoline (75%) and indole (7.7%). No sultam was recovered, and no dihydropyrindine or styrene was detected.

Flash Vacuum Pyrolysis of β-Phenethyl Azide. The column temperature was 500 °C and the inlet temperature 65 °C. Otherwise, the conditions were the same as those used in the sulfonyl azide pyrolyses. Gas chromatographic analysis of the product mixture showed the absence of dihydropyrindine, indoline, and indole. Only a number of very minor peaks were observed which were not identified.

Flash Vacuum Pyrolysis of 4-Methyl-β-phenethylsulfonyl Azide. (a) At 400 °C. The inlet temperature was 135 °C, the column temperature 400 °C, the initial pressure 3.70mmHg, rising to 3.80mmHg during the pyrolysis, the N_2 flow rate 31 mL/min (760mmHg), and the contact time 0.35 s. SO_2 was collected in the liquid-N_2 trap. The products were analyzed on an 8 ft × $^3/_{16}$ in. 10% OV-17 on Gas Chrom Q column, inlet temperature was 325 °C, the flow rate was 100 mL/min, and column temperature was held at 140 °C for 100 s and then programmed to 310 °C at a rate of 20 °C/min. *o*-Dichlorobenzene was the internal standard. The peak with retention time of 154 s was collected and identified as 4-methylstyrene by comparison of its IR, NMR, and mass spectra and GLC retention time with those of an authentic sample prepared by dehydrohalogenation of 4-methyl-β-phenethyl bromide with ethanolic KOH. The peak with a retention time of 399 s was collected and characterized as 6,7-dihydro-4-methyl-5*H*-1-pyrindine: IR (film) 3050 (w), 2940 (m), 2850 (w), 1605 (s), 1575 (w), 1445 (m), 1400 (m), 1315 (w), 1255 (w), 1220 (w), 1180 (w), 1085 (w), 1025 (w), 945 (w), 905 (w), 835 (s), 725 cm^{-1} (w); NMR ($CDCl_3$) δ 8.17 (d, $J_{2,3}$ = 5.6 Hz, 1 H), 6.79 (d, $J_{2,3}$ = 5.6 Hz, 1 H), 2.91 (m, 4 H), 2.21 (s, 3 H, CH_3), 2.06 (m, 2 H, H_6); mass spectrum (70 eV), *m/e* (relative intensity) 133 ($M^{+\cdot}$, 58), 132 (100), 118 (36), 117 (31). Anal. Calcd for $C_9H_{11}N$: C, 81.11; H, 8.33. Found: C, 81.12; H, 8.39. Picrate: mp 170–171 °C (lit.[33] 151 °C).

The peak with a retention time of 843 s was collected and was identical with the previously prepared 7-methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide. The quantitative results are summarized in Table I.

(b) At 650 °C. In addition to the methylstyrene and methyldihydropyrindine the following were isolated: 6-methylindoline (retention time = 452 s); IR (film) 3480 cm^{-1} (m); NMR ($CDCl_3$) δ 6.99 (d, $J_{4,5}$ = 7.5 Hz, 1 H, H_4), 6.51 (d, $J_{4,5}$ = 7.5 Hz, 1 H, H_5), 6.47 (s, 1 H, H_7), 3.53 (t, $J_{2,3}$ = 8.1 Hz, 2 H, H_2), 2.97 (t superimposed on br hump, 3 H, reduces to 2 H on shaking with D_2O, H_3 and NH), 2.24 (s, 3 H, CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 133 ($M^{+\cdot}$, 67), 132 (100), 131 (63), 130 (78), 119 (20), 118 (40), 77 (35). Anal. Calcd for $C_9H_{11}N$: C, 81.11; H, 8.33. Found: C, 81.10; H, 8.35. Picrate: mp 155–156 °C.

The peak with a retention time of 512 sec was due to 6-methylindole, identical with an authentic sample [*m/e* 131 ($M^{+\cdot}$, 87), 130 (100)]. The quantitative analyses are summarized in Table I.

Flash Vacuum Pyrolyses of 4-Chloro-β-phenethylsulfonyl Azide. These were carried out at 400 and 650 °C, as above. At 6 ft × $^3/_{16}$ in. 10% OV-17 on Gas Chrom Q column was used. *n*-Tridecane was the internal standard. 4-Chlorostyrene, identical with an authentic sample prepared by treatment of 4-chloro-β-phenethyl bromide with ethanolic KOH, had a retention time of 232 s. 4-Chloro-6,7-dihydro-5*H*-1-pyrindine: retention time = 423 s; NMR ($CDCl_3$) δ 8.4–7.9 (br s, 1 H, H_2), 7.03 (d, $J_{2,3}$ = 5.6 Hz, 1 H, H_3), 3.25–2.85 (m, 4 H, H_5, H_7), 2.4–1.8 (m, 2 H, H_6); NMR ($CDCl_3$ + 1 drop CF_3CO_2H) δ 8.51 (d, $J_{2,3}$ = 6.7 Hz, 1 H, H_2), 7.74 (d, $J_{2,3}$ = 6.7 Hz, 1 H, H_3), 3.65–3.10 (m, 4 H), 2.70–2.15 (m, 2 H); mass spectrum (70 eV), *m/e* (relative intensity) 155 ($M^{+\cdot}$, ^{37}Cl, 30), 153 ($M^{+\cdot}$, ^{35}Cl, 93), 152 (100), 118 (83), 117 (46), 63 (35). Anal. Calcd for C_8H_8ClN: C, 62.55; H, 5.25. Found: C, 62.46; H, 5.30. Picrate: mp 181–182 °C.

7-Chloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide had a retention time of 966 s. 6-Chloroindole (mp 88–89 °C), identical with an authentic sample, had a retention time of 608 s. 6-Chloroindoline: retention time = 558 s; IR (film) 3390 cm^{-1} (m); NMR ($CDCl_3$) δ 6.95 (d, $J_{4,5}$ = 7.5 Hz, 1 H, H_4), 6.61 (dd, $J_{4,5}$ = 7.5 Hz, $J_{5,7}$ = 1.0 Hz, 1 H, H_5), 6.56 (s superimposed on 6.61 doublet, 1 H, H_7), 3.56 (t, $J_{2,3}$ = 8.5 Hz, 2 H, H_2), 2.95 (t superimposed on a br hump, $J_{2,3}$ = 8.5 Hz, 3 H, reduces to 2 H on shaking with D_2O, H_3 NH); mass spectrum (70 eV), *m/e* (relative intensity) 156 ($M^{+\cdot}$, ^{37}Cl, 35), 154 ($M^{+\cdot}$, ^{35}Cl, 100), 153 (87), 119 (43), 118 (80), 40 (60). Anal. Calcd for C_8H_8ClN; C, 62.55; H, 5.25. Found: C, 62.48; H, 5.40.

The quantitative results are summarized in Table I.

Flash Vacuum Pyrolyses of 4-Methoxy-β-phenethylsulfonyl Azide. These were carried out at 400 and 650 °C, as usual. *n*-Pentadecane was used as the internal standard. 4-Methoxy-6,7-dihydro-5*H*-1-pyrindine (retention time = 474 s): NMR ($CDCl_3$) δ 8.27 (d, $J_{2,3}$ = 5.8 Hz, 1 H, H_2), 6.54 (d, $J_{2,3}$ = 5.8 Hz, 1 H, H_3), 3.85 (s, 3 H, OCH_3), 3.2–2.6 (m, 4 H, H_5, H_7), 2.3–1.9 (m, 2 H, H_6); mass spectrum (70 eV), *m/e* (relative intensity) 149 ($M^{+\cdot}$, 100), 148 (95), 134 (48), 118 (31). Anal. Calcd for $C_9H_{11}NO$: C, 72.46; H, 7.43. Found: C, 72.45; H, 7.44. Picrate: mp 195–196 °C. Anal. Calcd for $C_9H_{11}NO{\cdot}C_6H_3N_3O_7$: C, 47.63; H, 3.73. Found: C, 47.72; H, 3.72.

7-Methoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxide had a retention time of 885 s. 6-Methoxyindoline (retention time = 632 s) was identical with an authentic sample kindly supplied by Dr. Hiteo Iida. The quantitative analysis results are summarized in Table I.

Flash Vacuum Pyrolysis of 2-Phenylpropanesulfonyl Azide. An 8 ft × $^3/_{16}$ in. 10% OV-17 on Gas Chrom Q column was used. The inlet temperature was 325 °C, the column temperature was held at 135 °C for 100 s and programmed to 290 °C at a rate of 20 °C/min. *n*-Dodecane was the internal standard. α-Methylstyrene, identical with an authentic sample, had a retention time of 201 s. The peak with a retention time of 377 s was collected as a colorless liquid which was found to be a mixture of 6- and 7-methyl-6,7-dihydro-5*H*-1-pyrindine by comparison with individual authentic isomers (see below). The ratio of the 6- to the 7-methyl isomers was determined to be ca. 4:1 by measuring the relative areas of the methyl peaks in the NMR spectrum of the

(32) Prelog, V.; Szpilfogel, S. *Helv. Chim. Acta* **1945**, *28*, 1684.

(33) Colonge, J.; Dreux, J.; Thiers, M. *Bull. Soc. Chim. Fr.* **1959**, 1461.

mixture ($CDCl_3$ + 1 drop CF_3CO_2H): δ 1.25 for the 6-Me isomer, δ 1.44 for the 7-Me isomer.

3-Methylindoline, identical with an authentic sample, picrate (mp 146–148 °C), had a retention time of 420 s. 4-Methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide had a retention time of 840 s. The quantitative results are summarized in Table I.

6-Methyl-6,7-dihydro-5*H*-1-pyrindine. A mixture of 5- and 6-methyloctahydropyrindines (12.0 g)[19] was dehydrogenated with 10% Pd-C in mesitylene. The mixture of 5- and 6-methyl-6,7-dihydro-5*H*-1-pyrindines was obtained (72%): bp 101–104 °C (35 mm). Attempted separation of the isomers on a variety of gas chromatographic columns (OV-17, Versamid 900, diethylene glycol succinate) was unsuccessful. The mixture was converted to the picrates which were fractionally crystallized from 95% ethanol six times to give 6-methyl-6,7-dihydro-5*H*-1-pyrindine picrate: mp 137–137.5 °C (lit.[19] 135–136 °C). Decomposition with NH_4OH gave the free base: NMR ($CDCl_3$ + 1 drop CF_3CO_2H) δ 8.46 (d, $J_{2,3}$ = 5.0 Hz, 1 H, H_2), 8.26 (d, $J_{3,4}$ = 8.0 Hz, 1 H, H_4), 7.70 (dd, $J_{2,3}$ = 5.0 Hz, $J_{3,4}$ = 8.0 Hz, 1 H, H_3), 3.6–2.4 (m, 5 H), 1.25 (d, J = 6.1 Hz, 3 H, CH_3); if CF_3CO_2H was not added to the $CDCl_3$ solution, H_2 gave a broad band at δ 8.2; mass spectrum (70 eV), *m/e* (relative intensity) 133 (M^+·, 100), 132 (96), 118 (92), 117 (32), 40 (24).

7-Methyl-6,7-dihydro-5*H*-1-pyrindine. To a solution of lithium diisopropylamide [from diisopropylamine (0.204 g) in THF (10 mL) at −25 °C and 2 N *n*-butyllithium in hexane (1.05 mL)] was added 6,7-dihydro-5*H*-1-pyrindine (0.24 g) at −25 °C with stirring under an atmosphere of dry N_2. After 30 min methyl iodide (0.30 g) in THF (2 mL) was added to the dark red solution at −25 °C. The solution, which became pale yellow, was allowed to come to room temperature and then evaporated. The yellow oil was purified by gas chromatography (single peak) on a 6 ft × $^3/_{16}$ in. 10% OV-17 on Gas Chrom Q column at 160 °C to give 7-methyl-6,7-dihydro-5*H*-1-pyrindine (retention time = 485 s); NMR ($CDCl_3$) δ 8.36 (d, $J_{2,3}$ = 5.4 Hz, 1 H, H_2), 7.46 (d, $J_{3,4}$ = 7.9 Hz, 1 H, H_4), 6.98 (dd, $J_{2,3}$ = 5.4 Hz, $J_{3,4}$ = 7.9 Hz, 1 H, H_3), 3.35–3.00 (m, 1 H, H_7) 2.97–2.78 (m, 2 H, H_5), 2.78–2.15 (m, 1 H, H_6), 1.84–1.54 (m, 1 H, H_6), 1.34 (d, J = 7.5 Hz, 3 H, CH_3); on addition of 1 drop of CF_3CO_2H the Me doublet moved downfield to δ 1.44; mass spectrum (70 eV), *m/e* (relative intensity) 133 (M^+·, 58), 132 (53), 118 (100), 117 (33). Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32. Found: C, 81.20; H, 8.29. Picrate: mp 128.5–129 °C (ethanol). Anal. Calcd for $C_9H_{11}N{\cdot}C_6H_3N_3O_7$: C, 49.73; H, 3.90. Found: C, 49.48; H, 3.88.

Flash Vacuum Pyrolysis of 1-Phenyl-2-propanesulfonyl Azide at 650 °C. The products were chromatographed on a column of silica gel to give a mixture of 6- and 7-methyl-6,7-dihydro-5*H*-1-pyrindine (17.3%) (6:7 = 4.3:1), β-methylstyrene (1.4%), and 3-methyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (8.4%).

At 400 °C the yields were 10.9% (6:7 = 5.8:1), 1.4%, and 14%, respectively.

Flash Vacuum Pyrolysis of Substituted 3,4-Dihydro-2,1-benzothiazine 2,2-Dioxides at 650 °C. These were carried out as described for the parent sultam. In no case was any styrene or dihydropyrindine detected, only indolines and indoles being formed. The results are summarized in Table II.

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Buffer Catalysis in the Hydrolysis of Picrylimidazole

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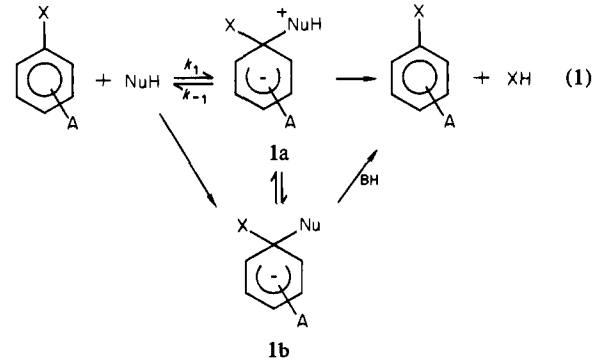
Abstract: The kinetics of the hydrolysis of picrylimidazole (S) was studied between pH 0.47 and 10.6 with different buffers at various concentrations. The reaction is strongly catalyzed by carboxylate and phosphate ions. Imidazole also catalyzes the reaction although it is a weak catalyst. At pH below 4 S starts to be protonated and the buffer-independent rate constant increases until it reaches a plateau. Rate constants for the base-catalyzed pathway are separated into the contribution of the rate for the protonated and unprotonated substrates. The Brønsted plots give slopes of 0.5 and 0.58, respectively. The mechanism of catalysis is discussed.

The reaction of amines with activated aromatic substrates was extensively studied during the past decade and important achievements regarding the mechanism of these reactions were obtained.[1] Most of the earliest studies have been done by conventional kinetics from which information about some of the elemental steps was obtained. The application of techniques for the measurement of fast reactions and the study of model reactions were definitive in firmly establishing the detailed mechanism of nucleophilic aromatic substitution and in particular the mechanism of the product-forming steps in reactions with amines as nucleophiles.[2] There are still some questions which remain to be answered, one of them pertains to the mechanism of the first step, namely, the addition of the nucleophile to the aromatic substrate to form the intermediate σ-complex **1a,b** (eq 1).



With neutral nucleophiles like amines, alcohols, or water, a proton must be removed at some point in the reaction coordinate to final products. Under conditions where the formation of the intermediate is rate determining, the intermediate **1a** may be so unstable that its formation is avoided through concerted catalysis. The diagonal pathway in eq 1 implies a transition state like **2** and has been suggested for the hydroxide ion catalysis observed in the reactions of amines,[3] under conditions where the formation of the

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