Institute, DHHS. We thank John G. Johansson for resynthesis of intermediate **46a**.

Registry No. **3**, 93349-61-2; **4**, 93349-62-3; **14**, 93349-63-4; **15**, 93349-64-5; **18**, 91-23-6; **19**, 90-04-0; **20**, 67291-62-7; **21**, 13398-79-3; **22**, 2876-17-7; **23**, 93349-65-6; **24**, 60855-15-4; **25**, 93349-66-7; **26**, 93349-67-8; **27**, 93349-68-9; **28**, 93383-20-1; **29**, 93349-69-0; **30**, 93349-70-3; **31**, 93349-71-4; **32**, 93349-72-5; **33**, 74783-59-8; **34**, 93349-73-6; **35**, 2944-49-2; **36a**, 50638-48-7; **37**, 93349-74-7; **40**, 93349-76-9; **43**, 93349-77-0; **44**, 93349-78-1; **45**, 93349-79-2; **46a**, 32178-63-5; **46b**, 93349-90-7; **47**, 93349-80-5; **48a**, 93349-81-6; **49a**, 93349-82-7; **49b**, 93349-75-8; **50**, 93349-83-8; **51**, 93349-84-9; **52**, 93349-85-0; **53**, 93349-86-1; **54**, 93349-87-2; **55**, 93349-88-3; **56**, 93349-89-4.

Solution and Flash Vacuum Pyrolyses of β-(3,5-Disubstituted-phenyl)ethanesulfonyl Azides. Sultam, Pyrindine, and Azepine Formation

Rudolph A. Abramovitch,*[1] William D. Holcomb,[2] W. Marshall Thompson, and Shigeo Wake[2]

Department of Chemistry and Geology, Clemson University, Clemson, South Carolina 29631-2586, and Department of Chemistry, University of Alabama, University, Alabama 35486

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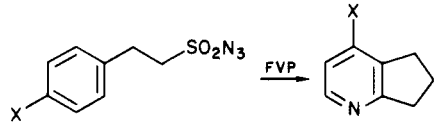
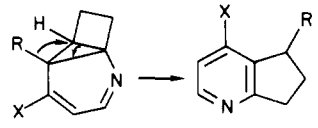
The solution and flash vacuum pyrolyses of β-(3,5-disubstituted-phenyl)ethanesulfonyl azides are reported. When R = Me, FVP results suggest that the substituents stabilize the intermediate leading to the 3,4-dihydro-2,1-benzothiazepine 2,2-dioxide (**6a**). A new product, 2-cyclopropyl-3,5-dimethylpyridine (**10**) is observed, and a modification is proposed in the mechanism proposed earlier[3] to account for the FVP of β-arylethanesulfonyl azides. No dihydropyrindine, which would have required a methyl migration, is observed. When R = Cl, Cl migration does occur and a mixture of 5*H*- and 7*H*-1-pyrindines is obtained, together with other products. When R = OCH_3, some methoxy migration occurs on FVP to give 6,7-dihydro-3,5-dimethoxy-5*H*-1-pyrindine. Monodemethoxylation to give 6-methoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**14**) also takes place and a possible mechanism is proposed. When R = CF_3 the main product on FVP at 300 °C is the fused azepine **19** in respectable yield. This is the first example of the isolation of an *N*-sulfonylazepine from the intramolecular reaction of a sulfonylnitrene and from a FVP.

The flash vacuum pyrolysis (FVP) of β-phenylethanesulfonyl azides (**1**) has been studied.[3] One of the most interesting products, formed in good yields at the higher column temperatures, is the dihydropyrindine ring system (**2**). A mechanism was proposed to explain this trans-



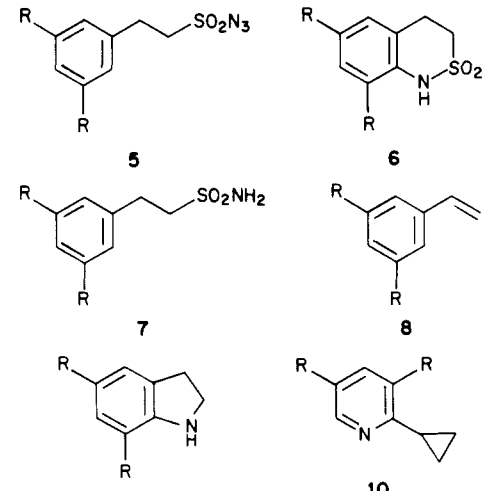
1 **2**

formation which, in its final stage, involved a 1,2-hydrogen shift accompanied by ring opening: **3** → **4** (R = H). The obvious question we asked ourselves was the following: assuming such a mechanism to be correct, what would happen when R ≠ H? It is this question we now address by studying the FVP of a series of β-(3,5-disubstituted-phenyl)ethanesulfonyl azides (R = Me, Cl, OMe, CF_3). The results obtained suggest a slight modification in the mechanism proposed[3] for the transformation **1** → **2**.



3 **4**

The sulfonyl azides **5** (R = Me, Cl, OMe, CF_3) were synthesized by standard methods (see Experimental Section).



a, R = Me; **b**, R = Cl; **c**, R = OMe; **d**, R = CF_3

Thermolysis of **5a** in Freon 113 at 135 °C gave the expected sultam 6,8-dimethyl-3,4-dihydro-2,1-benzothiazepine 2,2-dioxide (**6a**), together with the hydrogen abstraction product, β-(3,5-dimethylphenyl)ethanesulfonamide (**7a**) (7%). FVP of **5a** at 400 °C gave **6a** (46–61.5%), 3,5-dimethylstyrene (**8a**) (3.8%), and 5,7-dimethylindoline (**9a**) (trace). On the other hand FVP at 650 °C led to a decreased yield (20.5%) of **6a**, a much larger amount (14.8%) of **9a**, and a novel product for such reactions,

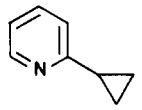
(1) To whom correspondence should be addressed at Clemson University.
(2) Work done at the University of Alabama.
(3) Abramovitch, R. A.; Holcomb, W. D.; Wake, S. *J. Am. Chem. Soc.* **1981**, *103*, 1525.

0022-3263/84/1949-5124$01.50/0 © 1984 American Chemical Society

2-cyclopropyl-3,5-dimethylpyridine (**10**). An authentic sample of **10** was prepared (49%) from 3,5-dimethylpyridine and cyclopropyllithium. No dihydropyrindine was detected. Styrene **8a** was also formed but not analyzed quantitatively.

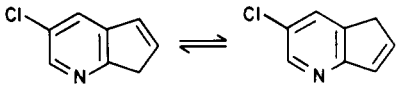
In view of the formation of **10** we have reinvestigated the FVP of the parent sulfonyl azide (**5**, R = H) at 650 and 750 °C. A very minor peak was observed by gas chromatographic analysis which had the same retention time as that of authentic 2-cyclopropylpyridine (**11**)[4] but was present in too low a concentration (<0.1%) to permit isolation and definitive identification (GC/MS not available to us at that time).

FVP of authentic 2-cyclopropylpyridine (**11**) at 650 °C gave a number of minor, uncharacterized products (41.9% of **13** recovered) but no dihydropyrindine (**2**, X = H), eliminating the possibility that this pathway is the source of **2** obtained in the pyrolysis of **1**. Similarly, FVP of **10** at 650 °C gave unchanged starting material. On the other hand, FVP of **6a** gave, as expected,[3] 5,7-dimethylindoline (**9a**) (72.5%).



11

Solution thermolysis of **5b** in Freon 113 at 135 °C for 40 h gave sultam **6b** (18.7%), sulfonamide **7b** (17.2%), recovered **5b** (24.3%), and much black solid. FVP of **5b** at 400 °C gave less sultam **6b** (13.4%), some styrene **8b** (1.9%), very little (0.6%) 5,7-dichloroindoline (**9b**), and a mixture of 3-dichloro-5*H*-1-pyridine (**12**) and 3-chloro-7*H*-1-pyridine (**13**) (total yield 12%). FVP at 650 °C gave **6b** (4.8%), **8b** (2.4%), **9b** (2.7%), and **12** + **13** (43.9%). The pyrindines **12** and **13** were actually obtained



13 **12**

as the hydrochlorides from the FVP, the free bases were liberated with sodium carbonate, and the mixture, mp 58–59 °C, was analyzed. That indeed we were dealing with an equilibrium mixture **12** ⇌ **13** was indicated by a consideration of the NMR spectrum of the products. In $CDCl_3$, these exhibited two doublets ($J_{2,4}$ = 2.5 Hz, 1 H) at δ 8.39 and 8.28 corresponding to the α-proton of the pyridine ring (H_2) in both tautomers, two doublets ($J_{2,4}$ = 2.5 Hz, 1 H) at δ 7.65 and 7.53 (pyridine γ-proton, H_4), and peaks at δ 7.07–6.67 (m, 2 H, CH=CH) and 3.60–3.30 (m, 2 H, CH_2). When the freshly prepared solution is allowed to stand the ratio of the areas of the peaks at δ 8.39 and 8.28 decreases from 3.9:1 to 1.5:1 (while still integrating for 1 H), as does also that of the peaks at 7.65 and 7.53. Decoupling of the multiplet centered at 6.77 resolves the multiplet at δ 3.60–3.30 into two singlets at δ 3.40 and 3.37. Similarly, irradiation at 7.58 ppm collapses the doublet at δ 8.39 and 8.26 into singlets. On the reasonable assumption that **12** + **13** arise from the dehydrohalogenation of the product **4** formed from **3** (or its equivalent), then the product initially formed should be **13** that then tautomerizes to **12**. Hence, the peaks at δ 8.39, 7.65, and 3.40 may be attributed to H_2, H_4, and H_7, respectively, in **13**, while those at δ 8.28, 7.53, and 3.37 may be attributed to H_2, H_4, and H_5 in **12**. The tautomerism of 5*H*- and 7*H*-1-pyrindines has already been reported.[5]

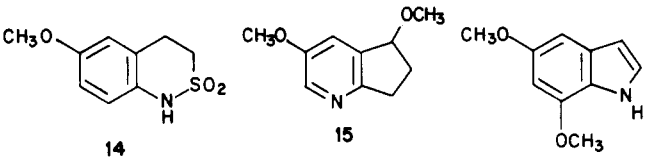
(4) Kurtz, W. *Chem. Ber.* **1975**, *108*, 3415.

Table I. FVP[a] of β-(3,5-Dimethoxyphenyl)ethanesulfonyl Azide (5c)

column temp, °C	recovered azide, %	yield, %					
		6c	**8c**	**9c**	**14**	**15**	**16**
250	45.5	28.2					
450	5.6	58.5					
650		11.7	1.2	1.2	3.2	3.7	0.4

[a] No carrier gas, 0.025 mmHg, 4 h.

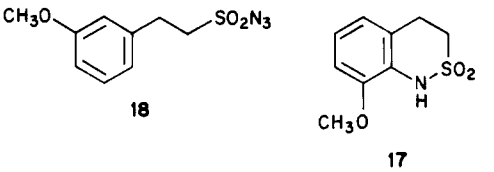
Solution decomposition of **5c** in Freon 113 proceeded uneventfully (see Experimental Section), the best conditions being thermolysis at 185 °C for 48 h to yield **6c** (75.8%) and only a trace of starting azide. Flash vacuum pyrolysis, on the other hand, gave interesting (and some unexpected) results which are summarized in Table I (about thirty products were detected by gas chromatography; only the most important ones are mentioned). Under the most favorable conditions, FVP at 450 °C gave a 58.5% yield of sultam **6c**, appreciably lower than that obtained by thermolysis in Freon. No SO_2 extrusion products were formed at that temperature. At 650 °C, a number of new products are formed. 5,7-Dimethoxyindole (**16**) arises by dehydrogenation of **9c**.[3]



14 **15** **16**

Interestingly, 6,7-dihydro-3,5-dimethoxy-5*H*-1-pyrindine (**15**) is also obtained. Thus, migration of a methoxy group in **3′** (R = OMe) (or its equivalent) does take place to give **27** (R = OMe) (Scheme I). The structure of **15** was confirmed by its NMR spectrum, which exhibited peaks for the pyridine α-(δ 8.18) and γ-protons (δ 7.22), for H_5 (δ 4.83, t, J = 6.2 Hz), and for the two methoxy groups (δ 3.85, 3.43) and multiplets for the two methylene groups (δ 2.91, 2.34).

Perhaps the most interesting (and unexpected) product was that of monodemethoxylation **14**. The structure proposed was confirmed by the synthesis of both 6- (**14**) and 8-methoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**17**) [by the solution thermolysis of β-(3-methoxyphenyl)ethanesulfonyl azide (**18**)] and a comparison of their NMR spectra: the main product (**14**) was identical with that obtained by FVP of **5c** and exhibited a 2 H singlet (60 MHz) at δ 6.74 and a 1 H singlet at δ 6.71. The 8-methoxy derivative **17** exhibited a 3-H multiplet at δ 6.80.



18 **17**

The band for NH in **17** resonated at slightly lower field (δ 6.80, exchangeable, overlapping with the aromatic protons) than does that in **14** (δ 6.62). More important is the fact that the OCH_3 group in **17** resonated at lower field (δ 3.86) than that in **14** (δ 3.77), similar to the order of absorbances of 7- and 5-methoxyindole, respectively. Attempted $Eu(FOD)_3$ shift reagent studies were inconclusive, however [Δ δ (ppm)/equiv of $Eu(FOD)_3$ in **14** H_5

(5) Robinson, M. M. *J. Am. Chem. Soc.* **1958**, *80*, 6254. Reese, C. B. *Ibid.* **1962**, *84*, 3979. Bergson, G.; Weidler, A.-M. *Acta Chem. Scand.* **1962**, *16*, 2464. Anderson, A. G., Jr.; Ammon, H. L. *Tetrahedron Lett.* **1966**, 2579.

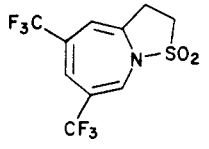
= 0.216, H_7 = 0.072, H_8 = 0.072, in **6c** H_5 = 0.232, H_7 = 0.136] because the reagent appears to complex the SO_2 rather than with nitrogen in these lactams.

β-[3,5-Bis(trifluoromethyl)phenyl]ethanesulfonyl azide (**5d**) was synthesized in the usual way:

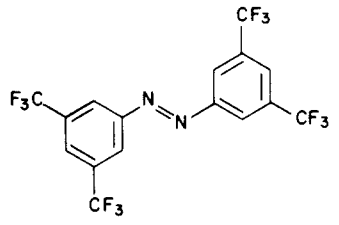
$$3,5\text{-}(CF_3)_2C_6H_3NH_2 \rightarrow ArBr \rightarrow ArCH_2CH_2OH \rightarrow ArCH_2CH_2Br \rightarrow ArCH_2CH_2SO_3Na \rightarrow ArCH_2CH_2SO_2Cl \rightarrow \mathbf{5d}$$

The only difficulty was experienced in the conversion of the aryl halide to the ethyl alcohol. Initially, the arylmagnesium *iodide* was prepared and treated with oxirane: the desired alcohol was formed in only 2.5% yield, the main product being 2-iodoethanol (attack of oxirane by iodide ion). The bromide, however, gave the desired product (ca. 70% yield). The arylmagnesium iodide reacted normally with acetaldehyde and with acetone.

Solution decomposition of **5d** proceeded very poorly. At 135 °C for 216 h no product could be identified and 59.8% of starting azide was recovered. At 150 °C for 60 h, 62.1% of **5d** was still recovered but a 3.9% yield of the *N*-sulfonylazepine **19** was isolated. The yield of **19** increased to 8.2% when **5d** was heated in Freon 113 at 180 °C for 72 h. No other products could be isolated and no azide was recovered. Contrary to what had been observed in the reaction of azidoformates with nitrobenzene in the presence of trifluoroacetic acid,[6] thermolysis of **5d** at 135 °C for 72 h in the presence of TFA did not yield any **19** or **6d**.



19

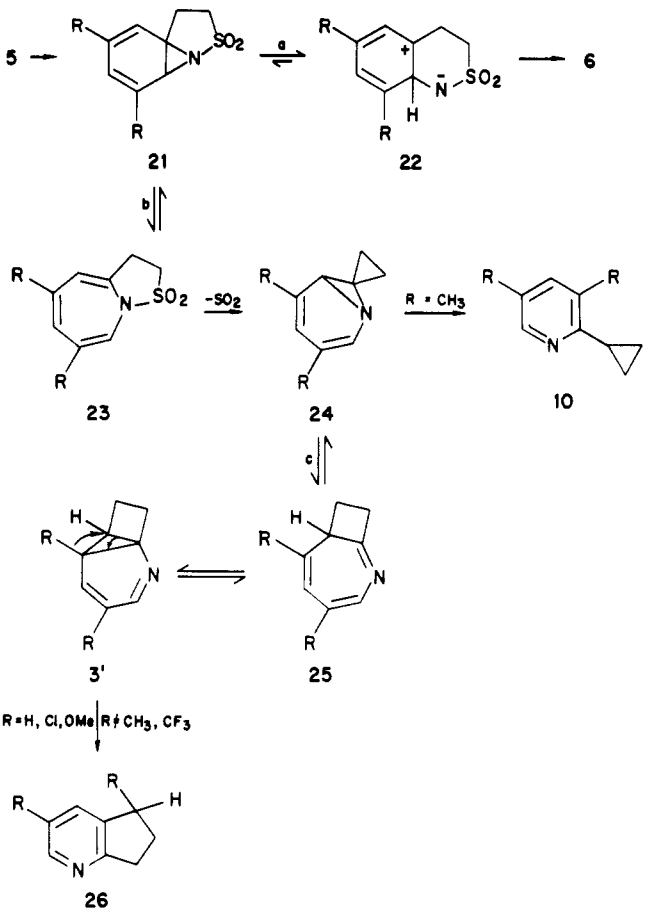


20

FVP was much more promising. At 250 °C a 3.6% yield of **19** was isolated, together with a trace of the azo compound **20**.[7,8] At 400 °C, **19** (16.2%) and a trace of **20** were formed. At 300 °C, **19** (48.9%), **20** (0.2%), and the six-membered sultam (**6d**) (6.3%) were isolated, together with starting azide (8%). Interestingly, FVP of **19** *did not* give **6d** under most of the conditions investigated (up to 650 °C), nor was any pyrindine derivative isolated at higher temperatures. Some azepine **19** (11.3%) survived FVP at temperatures up to 400 °C, and a trace of **6d** was detected by GC/MS after FVP at 375 °C. Only tars were isolated from the FVP at 500 °C. An authentic sample of **20** was made by the oxidation (I_2/MeOH) of the hydrazo compound (see supplemental material).

When **19** was treated with 2 equiv of 1-(diethylamino)-1-propyne in hexane at room temperature a mixture of at least 10 products was formed, one of which was 2:1 ynamine to azepine adduct (GC/MS, *m/e* 541, $M^{\cdot+}$). No 1:1 adduct was detected. A red crystalline material isolated by column chromatography on silica gel was shown by TLC to be a mixture of two components which could not be resolved further owing to the decomposition of the product on silica. Neutral alumina did not resolve the components. The main component of this substance exhibited what appeared to be a parent ion at *m/e* 571.

Scheme I



Discussion

There are a number of interesting aspects to the FVP of β-(3,5-dimethylphenyl)ethanesulfonyl azide (**5a**). The unprecedented formation of **10** (not a precursor of **9a**) suggests that a modest modification of the proposed scheme[3] for the genesis of **9** may be in order (Scheme I). The nitrene is first formed without participation[10] and adds, as usual, to give **21**. This can either ring expand to the azepine or ring open to a dipolar or diradical intermediate (the former is shown in Scheme I) which then isomerizes to **6**. This explains an additional notable feature of this FVP, namely that in this case, where R group migration leading to a dihydropyrindine is *not* observed, an appreciable amount of sultam **6** (R = Me) is formed even at 650 °C, whereas when R = H no sultam is observed at that temperature. The developing positive charge (or radical) in **22** would be stabilized appreciably by the two methyl groups, shifting the process in this direction. Loss of SO_2 from **23** and electrocyclization could lead to **24** from which **10** could readily form. Alternatively, pathway c would give **25** and thence **3′**. If migration of R can occur (R = H, Cl, OMe—vide infra) the dihydropyrindine **26** is obtained. Otherwise **3′** reverts to **25** and **24** and thence to **10** (or gives the tars that are invariably observed). Another possible route to **10** or to **26** (Scheme II) is also

(6) Takeuchi, H.; Koyama, K. *J. Chem. Soc., Chem. Commun.* **1982**, 226.

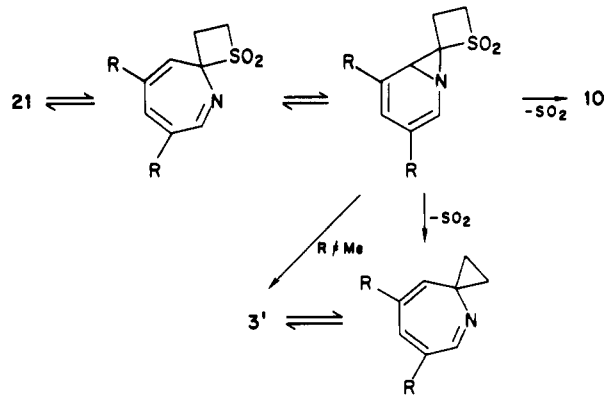
(7) Zalesskaya, I. M.; Blakitnyi, A. N.; Saenko, E. P.; Fialkow, Yu. A.; Yagupol'skii, L. M. *Zh. Org. Khim.* **1980**, *16*, 1194.

(8) Attempted deoxygenation of 3,3′,5,5′-tetrakis(trifluoromethyl)azoxybenzene[9] with PCl_3 in boiling chloroform (overnight) gave recovered starting material (97.8%). On the other hand, oxidation of the hydrazo compound with iodine in boiling methanol[7] gave the desired **20** (96.4%).

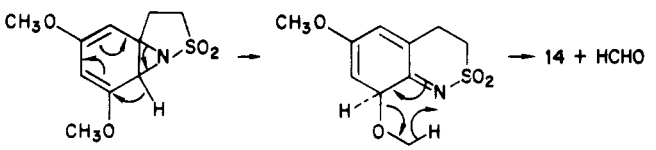
(9) Bunce, N. J.; Schoch, J.-P.; Zerner, M. C. *J. Am. Chem. Soc.* **1977**, *99*, 7986.

(10) McManus, S. P.; Smith, M. R.; Abramovitch, R. A.; Offor, M. N. *J. Org. Chem.* **1984**, *49*, 683.

Scheme II

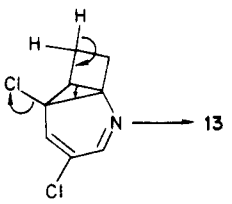


Scheme III



conceivable[11] but seems somewhat less likely.

Chlorine migration in 3′ (R = Cl) would lead to **26** (R = Cl) which would eliminate HCl to give **13**. Alternatively, **13** could be formed directly from 3′:



The FVP of **5c** at 650 °C provided some noteworthy results, including evidence that a methoxy group in **3** (or rather 3′) does migrate so that the expected dihydropyrindine is formed (3′ → **26**, Scheme I). The yields are low since alternate reaction pathways (ca. 30 products formed) are available. Some products which may have been formed in very small quantities but were not detected include 3-methoxy-7*H*-pyrindine and its 5*H* tautomer and 2-cyclopropyl-3,5-dimethoxypyridine. A number of attempts were made to synthesize an authentic sample of the latter: addition cyclopropyllithium to 3,5-dimethoxypyridine (or its *N*-oxide) and reaction of cyclopropyl radical (from the Ag(I)-catalyzed oxidative decarboxylation of cyclopropanecarboxylic acid[12,13]) with 3,5-dimethoxypyridinium ion even in the presence of a 10-fold excess of silver salt,[14] but no cyclopropylpyridine derivative could be detected, even by GC/MS. It appears that 3,5-dimethoxypyridine and the corresponding pyridinium salt are not electrophilic enough to react with either the cyclopropyl anion or the radical (nucleophilic[13]), respectively. The yield of **6c** obtained at 650 °C is still fairly high for a FVP at this temperature, which suggests that the methoxy substituents probably also stabilize **23** (R = OMe) (or the radical equivalent).

The unexpected loss of a methoxy group (resulting in the formation of the monomethoxylated sultam **14**) has not been encountered previously in FVP, though it is known in mass spectrometry.[15] It may be rationalized as in Scheme III, but alternate stepwise radical (or dipolar e.g. **22**) pathways are possible.

Table II. New Sulfonyl Azides

sulfonyl azide	yield, %	mp, °C
β-(3,5-dimethylphenyl)ethane	70	49.5–50
β-(3,5-dichlorophenyl)ethane	97.6	79–80
β-(3,5-dimethoxyphenyl)ethane	78.7	39–41
β-(3-methoxyphenyl)ethane	94.7	66–67
β-[3,5-bis(trifluoromethyl)phenyl]ethane	90.2	48–49

Table III. New Sulfonamides

sulfonamide	yield, %	mp, °C
β-(3,5-dimethylphenyl)ethane	85	98.5–99
β-(3,5-dichlorophenyl)ethane	82	124.5–125
β-(3,5-dimethoxyphenyl)ethane	72.1	93–94
β-[3,5-bis(trifluoromethyl)phenyl]ethane	43.4	168–169

Solution thermolysis and, better still, FVP of **5d** at 300 °C gave the *N*-sulfonylazepine **19**. This is the first example of the isolation of an azepine from the *intra*molecular reaction of an sulfonylnitrene, though *inter*molecular reaction *in solution* has occasionally led to their isolation.[16] It is also the first example of the isolation of an *N*-sulfonylazepine from a FVP. While *N*-sulfonylazepines are usually unstable at temperatures much above 100 °C[16a] they are stabilized by electron-withdrawing groups.[17] It has been suggested[18] that electron-withdrawing substituents would shift the equilibrium from the azepine to the aza[4.1.0]heptadiene isomer.[19] That the product formed was not 3,5-bis(trifluoromethyl)-10-thia-1-azatricyclo-[5.3.0.$0^{2,7}$]deca-3,5-diene 10,10-dioxide (**21d**) was confirmed by its ultraviolet absorption spectrum in hexane (λ_{max} 222 and 354 nm), typical[18] of azepines.

It was hoped that the isolation of **19** would allow us to test the hypothesis [Scheme I, **19** = **23** (R = CF_3)] that **23** is actually an intermediate in the formation of **6**, **10**, and **26**. Unfortunately, as pointed out earlier, **19** proved to be relatively stable to FVP conditions, most of it being recovered at temperatures below 350 °C. At 375 °C a trace of **6d** was actually observed, and at 400 °C and higher GC/MS showed the presence of small quantities of SO_2 extrusion products. Column chromatography failed, however, to yield material in sufficient quantities for analysis. Proof (or otherwise) of the pivotal role of **23** in Scheme I thus awaits the isolation of a more cooperative fused *N*-sulfonylazepine. The sultam **6d** also formed on FVP at 300 °C most probably arises directly from **21** initially formed *before* its isomerization to **23**. Azepine **19** was, not unexpectedly (since both reactants are electron poor), found to be unreactive toward acrylonitrile up to 205 °C. Complex products were formed with 1-(diethylamino)-1-propyne but their structures could not be unravelled.

A very small amount of azobenzene **20** formed by FVP of **5d** at 300 °C possibly may also arise from **21** by loss of

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ethylene and SO_2 (stepwise or concerted) to give the arylnitrene that dimerizes. A sequence involving the isomerization of a sulfonylnitrene to an *N*-sulfonylaniline followed by loss of SO_2 to give an arylnitrene that dimerizes has been postulated to explain the formation of an azobenzene from an arenesulfonyl azide.[20]

Experimental Section

Melting points are uncorrected.

Sulfonyl Azides. A typical sequence is described below. The azides were prepared from the corresponding sulfonyl chlorides, and unless there is something special to the procedure the synthesis and characterization of the sulfonyl azides, sulfonyl chlorides, and their precursors, as well as the primary sulfonamides are described in detail in supplementary pages following this article. New sulfonyl azides are listed in Table II, sulfonamides in Table III.

Solution Thermolysis and Flash Vacuum Pyrolysis. Standard conditions employed in our laboratories were used and have already been described.[3,21]

β-(3,5-Dimethylphenyl)ethyl Bromide. To β-(3,5-dimethylphenyl)ethyl alcohol (34 g, 0.23 mol) was added dropwise with stirring phosphorous tribromide (22.0 g, 0.081 mol) at room temperature. The mixture was warmed slowly, boiled under reflux for 10 min, cooled, and distilled to give a cloudy liquid (bp 124–132 °C (31 mm)) which was clarified by passage through a column of neutral alumina (5 × 1 cm). The yield of bromide was 23.2 g (48%): NMR ($CDCl_3$) δ 6.88 (s, 1 H), 6.82 (s, 2 H), 3.54 (t, $J_{\alpha,\beta}$ = 3.7 Hz, 2 H), 3.08 (t, $J_{\alpha,\beta}$ = 3.7 Hz, 2 H), 2.29 (s, 3 H); mass spectrum, $M^{\cdot+}$ *m/e* 214, 212. Anal. Calcd for $C_{10}H_{13}Br$: C, 56.36; H, 6.15. Found: C, 56.36; H, 6.16.

β-(3,5-Dimethylphenyl)ethanesulfonyl Chloride. To an aqueous solution (200 mL) of anhydrous sodium sulfite (16.0 g, 0.127 mol) was added β-(3,5-dimethylphenyl)ethyl bromide (20.0 g, 0.094 mol) and the solution was boiled under reflux with stirring for 24 h. The solution was evaporated to dryness, and the solid was air dried, pulverized, and dried in vacuo (30 mmHg) at 60 °C. This white solid was placed in a flask, dry benzene (300 mL) was added followed by dimethylformamide (2.0 g), and then thionyl chloride (11.9 g, 0.100 mol) was added dropwise. The mixture was boiled under reflux with stirring for 4 h, cooled, and filtered through Celite, and Celite was washed with dry benzene (2 × 10 mL) and concentrated to give a white solid. Recrystallization from light petroleum (bp 30–60 °C) at −78 °C gave the sulfonyl chloride (13.2 g, 61%): mp 48–49 °C; IR (KBr) 1360 (s), 1170 cm^{-1} (s); NMR ($CDCl_3$) δ 6.93 (s, 1 H), 6.83 (s, 2 H), 3.89 (m, 2 H), 3.22 (m, 2 H), 2.29 (s, 6 H); mass spectrum, *m/e* (relative intensity) 234 ($M^{\cdot+}$, ^{37}Cl, 4), 232 ($M^{\cdot+}$, ^{35}Cl, 12), 133 (56), 132 (100), 131 (24), 119 (48), 118 (14), 117 (54), 116 (12), 115 (27), 91 (39), 77 (20), 71 (13), 65 (19), 64 (22), 63 (16), 57 (20), 55 (15), 53 (14), 51 (19), 48 (15), 43 (21), 41 (34). Anal. Calcd for $C_{10}H_{13}ClO_2S$: C, 51.61; H, 5.63. Found: C, 51.75; H, 5.68.

β-(3,5-Dimethylphenyl)ethanesulfonyl Azide. β-(3,5-Dimethylphenyl)ethanesulfonyl chloride (11.0 g, 0.047 mol) was dissolved in acetone (100 mL) and cooled in an ice bath. Sodium azide (4.6 g, 0.073 mol) was dissolved in water (30 mL), cooled in an ice bath, and added portionwise with stirring to the chloride. The solution was stirred for 12 h, concentrated to ca. 40 mL behind a safety shield, and poured into water (100 mL). A white solid was extracted with ethyl acetate (2 × 100 mL), and the extract was washed with water (2 × 50 mL), aqueous sodium carbonate (5% w/v, 2 × 50 mL), and water (2 × 50 mL) and dried ($CaCl_2$). The ethyl acetate extract was evaporated on a warm water bath in vacuo behind a safety shield to give a tan solid which was recrystallized from light petroleum (bp 30–60 °C) to give colorless needles of β-(3,5-dimethylphenyl)ethanesulfonyl azide (70%): mp 49.5–50 °C; IR (KBr) 2120 (s), 1345 (s), 1150 cm^{-1} (s); NMR ($CDCl_3$) δ 6.93 (s, 1 H, C_4H), 6.86 (s, 2 H, C_2H and C_6H), 3.75–3.05 (m, 4 H, $C_\alpha H$ and $C_\beta H$), 2.29 (s, 6 H, CH_3); mass spectrum *m/e* (relative intensity) 239 ($M^{\cdot+}$, 4), 147 (17), 146 (15), 133 (31), 132 (100), 131 (28), 119 (25), 118 (13), 117 (59), 116 (12), 115 (30), 105 (26), 103 (10), 91 (36), 79 (12), 78 (10), 77 (26), 65 (18), 64 (20), 63 (10), 53 (11), 51 (12), 48 (11), 41 (37). Anal. Calcd for $C_{10}H_{13}N_3O_2S$: C, 50.19; H, 5.48. Found: C, 50.17; H, 5.48.

β-(3,5-Dimethylphenyl)ethanesulfonamide. β-(3,5-Dimethylphenyl)ethanesulfonyl chloride (0.62 g, 0.0027 mol) was dissolved in dry ether (50 mL) and ammonia gas passed through the solution with stirring for 2 h. The solution was filtered through Celite, and Celite was washed with ether (2 × 20 mL), and the combined ether solutions were dried ($CaCl_2$) and concentrated to yield a white solid which was recrystallized from light petroleum (bp 60–110 °C) to give the sulfonamide (0.48 g, 85%): mp 98.5–99 °C; IR (KBr) 3360 (m), 3270 (m), 1310 (s), 1150 cm^{-1} (s); NMR ($CDCl_3$) δ 6.90 (s, 3 H), 4.9–4.6 (br s, 2 H, exchanges with D_2O), 3.5–3.1 (m, 4 H), 2.31 (s, 6 H); mass spectrum, *m/e* (relative intensity) 213 ($M^{\cdot+}$, 7), 133 (21), 132 (100), 131 (10), 117 (30), 115 (9), 105 (9), 91 (14), 77 (9). Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.31; H, 7.09. Found: C, 56.40; H, 7.11.

Thermolysis of β-(3,5-Dimethylphenyl)ethanesulfonyl Azide. In Freon 113. The azide (4.023 g, 0.0168 mol) was divided into two portions and each portion added to Freon 113 (65 mL), and the solutions were flushed with nitrogen (dry, O_2 free), and then thermolized in glass lined steel bombs with stirring at 135 °C for 36 h. After the thermolysis the solution was light yellow and contained a large amount of white crystals mixed with a small amount of black tar. The two mixtures were combined, the vessels washed with ethyl acetate (2 × 30 mL), and the combined solutions evaporated onto neutral alumina (10 g) in vacuo. The decomposition products were chromatographed on a column of neutral alumina (2.3 × 25 cm) prepared in benzene. Elution with benzene–ethyl acetate (85:15 v/v) gave starting azide (0.33 g, 8.1%). Elution with benzene–ethyl acetate (1:1 v/v) gave a tan solid (1.63 g) which was sublimed (150 °C (5 μ)) to give 6,8-dimethyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (1.53 g, 43%): mp 188–189 °C; IR (KBr) 3260 (s), 1330 (s), 1170 cm^{-1} (s); NMR (acetone-d_6) δ 7.6 (br s, 1 H, exchanges with D_2O), 6.85 (s, 2 H), 3.31–3.15 (m, 4 H), and 2.20 (s, 6 H); mass spectrum, *m/e* (relative intensity) 212 (6), 211 ($M^{\cdot+}$, 55) 147 (35), 146 (100), 132 (39), 131 (37), 130 (18), 91 (11), 77 (13), 65 (10). Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20. Found: C, 56.90; H, 6.25.

Elution with ethyl acetate and ethyl acetate-ethanol (99:1 v/v) gave a tan solid (0.38 g) which was sublimed (80 °C (5 μ)) to give β-(3,5-dimethylphenyl)ethanesulfonamide (0.26 g, 7.2%) identical (infrared spectrum) with an authentic sample.

FVP at 400 °C. The azide (2.00 g, 8.37 mmol) was placed in the reservoir of the pyrolysis apparatus and pyrolyzed at a column temperature of 400 °C, with the preheater temperature at 56 °C, the inlet at 125 °C, and the exit at 250 °C. The pressure initially was 3.70 mm and rose to *ca.* 3.80 mm during the pyrolysis with a nitrogen flow of 25 mL/min (760 mmHg). The pyrolysis took 225 min and the contact time was 0.35 s. The liquid nitrogen trap contained sulfur dioxide identified by its odor. The pyrolysis products were washed from the trap with ethyl acetate (150 mL) and the trap was washed with ethyl acetate (2 × 15 mL). An insoluble precipitate separated (384 mg), mp >280 °C, and was filtered off. To the combined solution was added *n*-tetradecane (0.2728 g, 1.38 mmol) and the solution concentrated to *ca.* 5 mL by distillation through a 30-cm Vigreux column. Gas chromatographic analysis was performed on an OV-17 column (10%, 8 ft × $^3/_{16}$ in.) on Gas Chrom Q; inlet temperature 325 °C; detector 330 °C programmed from 130 °C (100 s isothermal hold) to 330 °C at 20 °C/min. The peak with retention time of 287 s was collected and identified as 3,5-dimethylstyrene by comparison of its MS and GLC retention time with those of an authentic sample prepared by the dehydrohalogenation of β-(3,5-dimethylphenyl)ethyl bromide with ethanolic potassium hydroxide.[22]

The balance of the solution was diluted with ethyl acetate and extracted with dilute HCl (0.3 N, 3 × 10 mL). The organic layer was dried (Na_2SO) and evaporated to yield a solid which was chromatographed on neutral alumina (2 × 20 cm). Elution with benzene (300 mL) gave a small amount of yellow oil (not investigated further). Elution with benzene–ethyl acetate (1:1 v/v) gave the sultam **6a** (0.807 g, 46%), mp 187–188 °C, identical with

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the sample obtained from the solution pyrolysis. The aqueous acidic extract was basified with Na_2CO_3 and extracted with ethyl acetate (2 × 25 mL) and the extract dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed on a column of silica gel (1.3 × 20 cm). Elution with benzene gave a small quantity of 5,7-dimethylindoline, identical (IR and GC) with the product fully characterized below.

FVP at 650 °C. The azide (1.0015 g, 4.19 mmol) was pyrolyzed as above but at 650 °C; all other settings were the same. The pyrolysis took 100 min. The liquid nitrogen trap contained sulfur dioxide identified by its odor. The pyrolysis products were washed from the cold finger with ethyl acetate (120 mL). The insoluble precipitate (40 mg) was filtered. The filtrate was extracted with dilute HCl (0.3 N, 2 × 20 mL). The ethyl acetate solution (A) was dried (Na_2SO_4). The aqueous solution was basified with Na_2CO_3 and extracted with ethyl acetate (2 × 20 mL). The ethyl acetate solution (B) was dried (N_2SO_4) and evaporated and the residue chromatographed on a column of silica gel (1.3 cm × 22 cm). Elution with petroleum ether (bp 30–60 °C)–benzene (1:5 v/v) and then elution with benzene gave a brown oil which was purified by gas chromatography [SE-30(10%) on Gas Chrom Q, 110 °C isothermal, He flow 50 mL/min] to give (a) 2-cyclopropyl-3,5-lutidine (t_R 510 s) (2.9%) identical (IR, NMR and mass spectra) with an authentic sample (vide infra). Picrate, mp and mmp 154–156 °C. (b) 5,7-Dimethylindoline (t_R 1050 s) (14.8%): IR (film) 3390 cm^{-1} (br); NMR ($CDCl_3$) δ 6.80 (s, 1 H, H_6), 6.67 (s, 1 H, H_4), 3.67–3.33 (m, 2 H, H_3), 3.20 (s, 1 H, NH, exchanges with D_2O), 3.13–2.8 (m, 2 H, H_2), 2.23 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3); mass spectrum, *m/e* (relative intensity) 147 ($M\cdot^+$, 82), 146 (100), 145 (49), 144 (33), 132 (23), 131 (31), 130 (42), 91 (12), 77 (14), 65 (14), 63 (10), 51 (17), 44 (68). Anal. Calcd for $C_{10}H_{13}N$: C, 81.63; H, 8.84. Found: C, 81.41; H, 8.88.

The ethyl acetate solution (A) was evaporated and the residue was chromatographed on a column of neutral alumina (1.3 × 20 cm). Elution with benzene–ethyl acetate (10:1 v/v, 160 mL) gave an unidentified oil (10 mg). Further elution with benzene–ethyl acetate (10:1 v/v, 300 mL) gave 6,8-dimethyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (0.18 g, 20.5%): mp 188–189 °C.

2-Cyclopropyl-3,5-dimethylpyridine. The apparatus was swept with dry nitrogen before and reaction. Freshly cut lithium (0.35 g, 0.05 mol) was suspended in dry ether (10 mL), and cyclopropyl bromide (3.0 g, 0.025 mol) in dry ether (5 mL) was added dropwise with stirring at such a rate as to keep the solution boiling. When lithiation was complete freshly distilled 3,5-lutidine (3.7 g, 0.035 mol) in dry toluene (10 mL) was added slowly with stirring. After addition, the reaction mixture was heated at 102 °C (inner temperature) for 9 h with stirring. After the mixture had cooled, water (10 mL) was added, and the aqueous layer was separated and discarded. The toluene solution was dried (Na_2SO_4), the solvent evaporated, and the residue distilled under reduced pressure to give 2-cyclopropyl-3,5-dimethylpyridine (1.8 g, 49%): bp 45–48 °C (0.05 mm); NMR ($CDCl_3$) δ 8.08 (br s, 1 H, H_6), 7.15 (br s, 1 H, H_4), 2.35 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 2.20–1.80 (m, 1 H, H_α), 1.08–0.78 (m, 4 H, H_β and H_α); mass spectrum, *m/e* (relative intensity) 147 ($M\cdot^+$, 85), 146 (100), 132 (92), 131 (37), 130 (19), 121 (18), 117 (22), 106 (7), 91 (8), 79 (8), 77 (19), 65 (10), 53 (8), 51 (10), 41 (5), 39 (15). Anal. Calcd for $C_{10}H_{13}N$: C, 81.63; H, 8.84. Found: C, 81.56; H, 8.90.

Picrate (from ethanol): mp 154–156 °C.

Flash Vacuum Pyrolysis of 6,8-Dimethyl-3,4-dihydro-2,1-benzothiazine 2,2-Dioxide. The sultam (0.205 g, 0.97 mmol) was pyrolyzed under the following conditions: inlet temperature 170 °C, column temperature 650 °C, exit temperature 250 °C, nitrogen flow rate 25 mL/min. Pyrolysis required 115 min. The products were washed with ethyl acetate (100 mL), the solution was extracted with dilute HCl (0.3 N, 3 × 10 mL), and the organic layer (A) (Na_2SO_4) was dried. The aqueous layer was basified with Na_2CO_3 and extracted with ethyl acetate (3 × 15 mL) and the ethyl acetate solution (B) dried (Na_2SO_4) and evaporated to give 5,7-dimethylindoline (47 mg, 72.5% based on recovered sultam) (IR, NMR). Solution (A) was evaporated to give starting sultam (0.112 g, 54.6%): mp 187–188 °C.

Decomposition of β-(3,5-Dichlorophenyl)ethanesulfonyl Azide. (a) In Freon 113. The azide (2.0 g, 7.15 mmol) in Freon 113 (40 mL) was degassed by a freeze–dry–thaw cycle (3 times) and heated in a pressure bomb at 135 °C for 40 h. At the end of this time, the light yellow solution contained a large amount of black solid. The vessel was washed with ethyl acetate (3 × 20 mL) and the combined washings and suspension were filtered from the black solid (0.54 g). The solvent was evaporated and the residue was chromatographed on a column of neutral alumina (1.3 × 25 cm). Elution with benzene gave starting azide (0.486 g, 24.3%). Elution with benzene–ethyl acetate (10:1 v/v) and benzene–ethyl acetate (5:1 v/v) gave 6,8-dichloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (0.255 g, 18.7% based on azide consumed): mp 156–157 °C (from benzene); NMR ($CDCl_3$) δ 7.28 (d, 1 H, J_m = 2 Hz, H_7), 7.07 (d, 1 H, J_m = 2 Hz, H_5), 6.90 (br s, 1 H, NH, exchanges with D_2O), 3.67–3.00 (m, 4 H, H_4 and H_3); mass spectrum, *m/e* (relative intensity), 255 ($M\cdot^+$, $^{37}Cl_2$, 35), 253 ($M\cdot^+$, ^{37}Cl + ^{35}Cl, 19), 251 ($M\cdot^+$, $^{35}Cl_2$, 28), 191 (2), 190 (4), 189 (12), 188 (19), 187 (19), 186 (27), 154 (3), 153 (18), 152 (10), 151 (53), 150 (3.5), 125 (5), 124 (2), 117 (9), 116 (5), and 89 (8). Anal. Calcd for $C_8H_7Cl_2NO_2S$: C, 38.11; H, 2.78. Found: C, 38.16; H, 2.81. Elution with benzene–ethyl acetate (2:1 v/v) gave β-(3,5-dichlorophenyl)ethanesulfonamide (0.239 g, 17.6% based on consumed starting azide): mp 124.5–125 °C (from benzene); NMR (acetone-d_6) δ 7.60–7.10 (m, 3 H, ArH), 6.53–5.83 (br s, 2 H, NH_2, exchanges with D_2O), 3.80–2.80 (m, 4 H, H_α and H_β); mass spectrum, *m/e* (relative intensity) 257 ($M\cdot^+$, $^{37}Cl_2$, 0.8), 255 ($M\cdot^+$, $^{37}Cl_4$ ^{35}Cl, 4.2), 253 ($M\cdot^+$, Cl_2, 5.9), 174 (67.6), 172 (100), 139 (9), 137 (23.5), 102 (17.6), and 75 (6.3). Anal. Calcd for $C_8H_9Cl_2NO_2S$: C, 37.81; H, 3.54. Found: C, 37.74; H, 3.61.

FVP at 400 °C. The azide (0.937 g) was pyrolyzed at 400 °C (preheater 90 °C, inlet 130 °C, exit 250 °C, pressure 10–15 mm, N_2 flow rate 25 mL/min, pyrolysis time 225 min). The cold finger was washed with ethyl acetate (120 mL). A precipitate was filtered (323 mg). The filtrate was extracted with dilute HCl (0.3 N, 2 × 15 mL) and the ethyl acetate solution (B) was dried (Na_2SO_4). The aqueous solution was basified with sodium carbonate and extracted with ethyl acetate (2 × 15 mL) (C), the solution dried (Na_2SO_4) and evaporated, and the residue resolved by preparative TLC (SiO_2, elution with ether–light petroleum bp 30–60 °C; 2:1 v/v). The zone with R_f 0.84 gave a mixture of 3-chloro-5*H*-1-pyrindine and 3-chloro-7*H*-1-pyrindine (10 mg). The ethyl acetate solution (B) was evaporated and the residue was chromatographed on a column of neutral alumina (1.3 × 20 cm). Elution with benzene gave a brown oil (20 mg) which was separated and purified by gas chromatography [SE-30 (10%) on Gas Chrom Q, 110 °C isothermal, He flow rate 50 mL/min]. The peak with a retention time of 240 s was collected and identified as 3,5-dichlorostyrene (11 mg, 1.9%) by comparison of its IR spectrum and GLC retention time with those of an authentic sample.[23] A small peak with the same retention time (25 min) as that of 5,7-dichloroindoline was also detected. Elution with benzene–ethyl acetate (10:1 v/v) gave 6,8-dichloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (113 mg, 13.4%): mp 155–156 °C. The insoluble precipitate (A) obtained above was partially dissolved in water (the aqueous solution was acidic and contained insoluble solid). It was basified with sodium carbonate and extracted with ethyl acetate. The solution was dried (Na_2SO_4) and the solvent was evaporated. The residue was chromatographed on a column of silica gel (1.3 × 21 cm). Elution with light petroleum (bp 30–60 °C)–benzene (2:1 v/v) gave 5,7-dichloroindoline (4 mg, 0.6%). Elution with light petroleum (bp 30–60 °C)–benzene (1:2 v/v) gave a mixture of 3-chloro-5*H*- and 3-chloro-7*H*-1-pyrindine (vide infra) (57 mg): mp 54–55 °C (combined total yield 67 mg, 12%).

FVP at 650 °C. The azide (1.032 g) was pyrolyzed as above except that the column temperature was 650 °C and the pyrolysis time 200 min. The cold finger was washed with ethyl acetate (120 mL) and the suspension was filtered from an insoluble precipitate (A) (413 mg). Workup as above gave the following. (a) 5,7-dichloroindoline (13 mg): NMR ($CDCl_3$) δ 7.00–6.80 (m, 2 H, ArH), 3.77–3.37 (m, 3 H, H_3 and NH, reduced to 2 H on addition of D_2O), 3.20–2.77 (m, 2 H, H_2); mass spectrum, *m/e* (relative intensity) 191 ($M\cdot^+$, $^{37}Cl_2$, 5), 190 (8), 189 ($M\cdot^+$, ^{37}Cl, ^{37}Cl, 35), 188 (40), 187 ($M\cdot^+$, $^{35}Cl_2$, 85), 186 ($M\cdot^+ - 1$, $^{35}Cl_2$, 56), 185 ($M\cdot^+ - 2$, $^{35}Cl_2$, 65), 153 (29), 152 (24), 151 (83), 125 (6.5), 124 (7.5), 123 (22), 117 (14), 116 (12), 115 (12), 114 (18), 89 (19), 76 (6). Anal. Calcd for $C_8H_7Cl_2N$: C, 51.09; H, 3.73. Found: C, 51.17; H, 3.75.

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(b) 3-Chloro-5*H*- and 3-chloro-7*H*-1-pyrindine (245 mg 43.9%): mp 58–59 °C (from light petroleum, bp 30–60 °C); NMR ($CDCl_3$) δ 8.39 and 8.28 (two d, 1 H, J_m = 2.5 Hz, H_2), 7.65 and 7.53 (two d, 1 H, J_m = 2.5 Hz, H_4), 7.07–6.67 (m, 2 H, CH=CH), 3.60–3.30 (m, 2 H, CH_2). The ratio of the doublets at both δ 8.39 and 8.2, and δ 7.65 and 7.53 was initially 3.9:1, but changed to 1.5:1 on keeping the solution. Irradiation at 6.77 ppm transforms the multiplets at δ 3.60–3.30 into two singlets at δ 3.37 and 3.40. Irradiation at 7.58 ppm changes the doublet at δ 8.39 and 8.28 into singlets; mass spectrum, *m/e* (relative intensity) 153 ($M^{\cdot+}$, ^{37}Cl, 10), 151 ($M^{\cdot+}$, ^{35}Cl, 30). Anal. Calcd for C_8H_6ClN: C, 63.37; H, 3.96. Found: C, 63.15; H, 4.02. The compounds were unstable and even on being kept in a sealed tube under nitrogen darkened in a few days at room temperature.

Thermolysis of β-(3,5-Dimethoxyphenyl)ethanesulfonyl Azide. In Freon 113 at 145 °C. A solution of β-(3,5-dimethoxyphenyl)ethanesulfonyl azide (0.25 g, 0.92 mmol) in dry Freon 113 (20 mL) was placed into a Fischer-Porter tube, and the solution degassed by the freeze–thaw method and heated at 145 °C for 240 h. The tube was allowed to cool, the contents were removed, and the tube was washed with hot ethyl acetate (2 × 15 mL). The combined solution and washings were evaporated in vacuo and the residue was chromatographed on a column of neutral alumina (15 cm × 10.0 cm) to give the following fractions: elution with benzene gave starting azide (200.7 mg, 80.4%); elution with $CHCl_3$ gave 6,8-dimethoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (36.3 mg, 16.3%): mp 158–159 °C (benzene); IR (KBr) 3220 (s), 1605 (s), 1310 (s), 1150 (s), 950 cm^{-1} (s); NMR ($CDCl_3$) δ 6.50 (bs, 1 H, exchanges with D_2O, NH), 6.39 (d, 1 H, J = 2.52, ArH), 6.27 (d, 1 H, J = 2.52 Hz, ArH), 3.83 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 3.43 (t, 2 H, J = 5.2 Hz, $ArCH_2$), 3.28 (t, 2 H, J = 5.2 Hz, SO_2CH_2). Anal. Calcd for $C_{10}H_{13}NO_4S$: C, 49.37; H, 5.39. Found: C, 49.30; H, 5.40.

The reaction was repeated under the following conditions: 165 °C, 48 h gave azide (65.6%) and sultam (19.5%); 185 °C, 48 h gave sultam (75.8%).

FVP. (i) At 250 °C. The azide (0.25 g, 0.922 mmol) was subjected to FVP under the following conditions: inlet temperature, 125 °C; pyrolysis temperature, 250 °C; pressure, 0.025 mm. The pressure stayed between 0.025–0.05 mm during the addition which took 1 h. The product was washed off the cold finger with hot ethyl acetate (3 × 25 mL), and the solution was evaporated in vacuo to give a light brown oil (248.6 mg) which was chromatographed on a neutral alumina column (1.5 × 10.0 cm) to give the following fractions: elution with hexane → hexane:benzene, 50:50 v/v, gave starting azide (113.7 mg, 45.5%); elution with hexane:benzene (50:50 v/v) → ether gave 6,8-dimethoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (63.3 mg, 28.2%) identical (IR and NMR) with the sultam obtained from solution thermolysis.

(ii) At 450 °C. This gave azide (5.6%) and sultam (58.5% from azide).

(iii) At 650 °C. Pyrolysis of the azide (1.00 g) gave a dark oil on evaporation of the ethyl acetate washings of the cold finger and was found to contain at least 30 products by GLC (3 ft × 2 mm ID, 10% Apiezon M on Gas Chrom Q, 100–120 mesh, He carrier, 30 mL/min, programmed run, 150 °C min, 250 °C 8 min). These could not be separated on a neutral alumina column without prior resolution into acidic, basic, and neutral components as follows: The dark oil was stirred with 5 N NaCH (50 mL) for 1 h at room temperature, diluted with water (150 mL), and extracted with ether (3 × 100 mL). The ethereal extracts were washed with 2 N hydrochloric acid (3 × 100 mL), dried ($MgSO_4$), and evaporated in vacuo to give the neutral components (FN) (81.8 mg). The basic solution from above was acidified with 2 N hydrochloric acid and extracted with chloroform (3 × 100 mL). The chloroform extracts were dried ($MgSO_4$) and evaporated in vacuo to give the acidic components (FA) (227.8 mg). The acid extracts from above were made basic with 5 N sodium hydroxide and extracted with ether (3 × 100 mL). The ethereal extracts were dried ($MgSO_4$) and evaporated in vacuo to give the basic components (FB) (49.3 mg).

FN was analyzed by GLC and GC/MS (4 ft × 2 mm ID, 5% Apiezon M on Gas Chrom Q, 100–120 mesh, He carrier, 30 mL/min, programmed run, 150 °C 2 min, 20 °C/min, 250 °C 15 min) to give the following: R_t = 3.7 min corresponded to 3,5-dimethoxystyrene (7.2 mg, 1.2%), identical (comparison of mass spectrum) with an authentic sample; R_t = 7.2 min corresponded to 5,7-dimethoxyindole (2.7 mg, 0.4%) identical (mass spectrum) with an authentic sample.

FA was chromatographed on a silica gel column (1.5 × 10.0 cm) and gave the following fractions: elution with ether gave 6,8-dimethoxy sultam **6c** (104.8 mg, 11.7%) identical (IR spectrum) with an authentic sample; elution with $CHCl_3$ gave 6-methoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (25.3 mg, 3.2%): mp 147–148 °C (benzene) identical (IR, NMR, MS, and mixed melting point) with an authentic sample prepared from β-(3-methoxyphenyl)ethanesulfonyl azide (vide infra).

FB was chromatographed on a basic alumina column (1.5 × 10.0 cm) to give the following fractions: elution with hexane gave 3,5-dimethoxy-6,7-dihydro-5*H*-1-pyridine (24.6 mg, 3.7%) as a colorless oil: bp 75–80 °C (0.01 mm); IR (film) 2940 (s), 1480 (s), 1290 (s), 1085 (s), 1085 (s), 1025 cm^{-1} (s); NMR ($CDCl_3$) δ 8.18 (bs, 1 H, H_α), 7.22 (d, 1 H, J = 2.7 Hz, H), 4.83 (t, 1 H, J = 6.2 Hz), 3.85 (s, 3 H), 3.43 (s, 3 H), 2.91 (m, 2 H), 2.34 (m, 2 H); mass spectrum (70 eV), *m/e* (relative intensity) 180 ($M^{\cdot+}$ + 1, 5.2), 179 ($M^{\cdot+}$, 50.0), 148 (100). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.17; H, 7.34; N, 7.77. Elution with hexane:benzene (50:50 v/v) gave 5,7-dimethoxyindoline (7.8 mg, 12%) identical (mass spectrum) with an authentic sample.

2-Nitro-3,5-dimethoxybenzyl Cyanide. To a solution of 3,5-dimethoxybenzyl cyanide[24] (1.77 g, 10.0 mmol) in acetic anhydride (45 mL) cooled to 0 °C was added in one portion $Cu(NO_3)_2 \cdot 3H_2O$ (1.21 g, 5.0 mmol) and the mixture was stirred for 4 h. The mixture was poured into ice–water (300 mL) and stirred for 30 min. The solid was filtered and recrystallized from methanol to give 2-nitro-3,5-dimethoxybenzyl cyanide (2.08 g, 93.6%): mp 75–77 °C; IR (film of molten sample) 2250 (w), 1605 (s), 1530 (s), 1340 (s), 1065 (s), 835 cm^{-1} (s); NMR ($CDCl_3$) δ 6.55 (d, 1 H, J = 3.0 Hz), 6.41 (d, 1 H, J = 3.0 Hz), 3.82 (s, 6 H), 3.74 (s, 2 H). Anal. Calcd for $C_{10}H_{10}N_2O_4$: C, 54.05; H, 4.54. Found: C, 54.07; H, 4.56.

5,7-Dimethoxyindole. To a solution of nitrile (5.00 g, 22.5 mmol) in ethyl acetate (150 mL) was added 10% Pd/C (2.5 g) and the mixture hydrogenated at 40 psi for 1 h, over which time the pressure dropped to 33 psi. The Pd/C was filtered and washed with ethyl acetate and the filtrate was concentrated in vacuo to give a green oil which solidified on standing. This was chromatographed on silica gel to give the following fractions: elution with benzene gave pale yellow crystals that were recrystallized from hexane:benzene (3:1 v/v) to give 5,7-dimethoxyindole (3.22 g, 80.8%) as colorless needles: mp 83–84 °C (lit.[25] mp 82 °C); IR (film of molten sample) 3440 (s), 1600 (s), 1330 (s), 1305 (s), 1140 (s), 1030 cm^{-1} (s); NMR ($CDCl_3$) δ 8.24 (bs, 1 H, exchanges with D_2O, NH), 7.07 (t, 1 H, J = 2.4 Hz), 6.68 (d, 1 H, J = 1.7 Hz), 6.44 (t, 1 H, J = 2.4 Hz), 6.35 (d, 1 H, J = 1.7 Hz), 3.89 (s, 3 H), 3.83 (s, 3 H); elution with benzene and then benzene:ether (50:50 v/v) gave a green oil (0.32 g) which was not characterized.

5,7-Dimethoxyindoline. To a solution of (0.89 g, 5.0 mmol) in 1 M BH_3·THF (10 mL) cooled to 0 °C was added dropwise trifluoroacetic acid (10 mL). The mixture was stirred at 0 °C for 30 min, water (1 mL) added, and the solution stirred for an additional 15 min. Most of the THF and TFA was removed in vacuo, the residue was treated with 10% NaOH (25 mL), and water was added (50 mL). The white solid which formed was filtered and recrystallized from hexane to give 5,7-dimethoxyindoline (0.86 g, 97.2%) as white needles: mp 52–53 °C; IR (film of molten sample) 3380 (s), 1610 (s), 1510 (s), 1330 (s) 1090 (s), 1040 (s), 860 (s), 800 cm^{-1} (s); NMR ($CDCl_3$) δ 6.39 (d, 1 H, J = 2.2 Hz), 6.30 (d, 1 H, J = 2.2 Hz), 3.79 (s, 3 H), 3.75 (s, 3 H), 3.54 (t, 2 H, J = 8.3 Hz), 3.18 (bs, 1 H, exchanges with D_2O, NH), 3.01 (t, 2 H, J = 8.3 Hz). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31. Found: C, 67.12; H, 7.36.

Thermolysis of β-(3-Methoxyphenyl)ethanesulfonyl Azide (18). A solution of **18** (223.2 mg, 0.925 mmol) in dry Freon 113 (25 mL) in a Fischer-Porter tube was degassed and heated to 150 °C for 256 h. After cooling and contents were removed and the tube washed with $CHCl_3$ (3 × 15 mL). The combined solutions

(24) Adams, R.; MacKenzie, S., Jr.; Loewe, S. *J. Am. Chem. Soc.* **1948**, *70*, 664.

(25) Mulligan, P. J.; La Berge, S. *J. Med. Chem.* **1970**, *13* 1248.

were concentrated in vacuo to give a dark oil which was chromatographed on a silica gel column: elution with hexane:benzene (2:3 v/v) gave azide (70.1 mg, 31.4%); elution with benzene:$CHCl_3$ (7:3 v/v) gave 8-methoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (30.5 mg, 15.5%): mp 157–157.5 °C (from hexane:benzene, 2:1 v/v); IR (KBr) 3300 (s), 1480 (s), 1070 (s), 920 cm^{-1} (s); NMR ($CDCl_3$) δ 6.80 (m, 5 H, ArH, NH), 3.86 (s, 3 H), 3.47 (t, 2 H, J = 5.2 Hz, CH_2SO_2), 3.29 (t, 2 H, J = 5.2 Hz, $ArCH_2$). Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20. Found: C, 50.58; H, 5.26. Elution with benzene:$CHCl_3$ (2:3 v/v) gave 6-methoxy-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (72.1 mg, 36.6%): mp 147–148 °C (from benzene); IR (KBr) 3270 (s), 1505 (s), 1315 (s), 1150 (s), 1030 (s), 930 cm^{-1} (s); NMR ($CDCl_3$) δ 6.74 (s, 2 H), 6.71 (s, 1 H), 3.77 (s, 3 H), 3.44 (t, 2 H, J = 4.8 Hz, CH_2SO_2), 3.29 (t, 2 H, J = 4.8 Hz, $ArCH_2$), 6.62 (bs, 1 H, exchanges with D_2O, NH). Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20. Found: C, 50.75; H, 5.24. This sultam was identical with the monodemethoxylated sultam obtained from the FVP of **5c** at 650 °C.

Thermolysis of β-[3,5-Bis(trifluoromethyl)phenyl]-ethanesulfonyl Azide. (a) In Freon 113 at 135 °C. A solution of **5d** (106.0 mg, 0.305 mmol) in dry Freon 113 (20 mL) was heated at 135 °C for 36 h. The tube was allowed to cool, the contents were removed, and the tube was washed with methylene chloride. The solution and washings were evaporated in vacuo to give a light yellow oil which was chromatographed on a silica gel column (1.5 cm × 10.0 cm). Elution with hexane:benzene (70:30 v/v) and hexane:benzene (60:40 v/v) gave starting azide (88.6 mg, 83.6%) as the only product isolated.

The reaction was repeated at 135 °C for 216 h which gave **5d** (59.8%) as the only product isolated. Another run was made with the addition of 25 equiv of trifluoroacetic acid at 135 °C for 72 h which gave **5d** (71.6%) as the only product isolated.

(b) In Freon 113 at 150 °C and at 185 °C. The azide was thermolized in Freon 113 at 150 °C for 60 h to give a dark brown oil which was chromatographed on a silica gel column (1.5 × 10.0 cm); elution with hexane:benzene (70:30 v/v) gave unchanged azide and 3,5-bis(trifluoromethyl)-10-thia-1-azabicyclo[5.3.0]deca-2,4,6-triene 10,10-dioxide (**19**) (3.9%) as light yellow needles: mp 105–106 °C; IR (KBr) 1680 (w), 1630 (w), 1350 (s), 1290 (s), 1160 (s), 1130 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 6.43 (s, 1 H, H_4), 6.13 (s, 1 H, H_2), 5.08 (s, 1 H, H_6), 3.10 (m, 4 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) proton decoupled δ 145.4 (s), 138.0 (q, J = 0.30 Hz), 133.8 (d, J = 1.3 Hz), 128.4 (d, J = 0.7 Hz), 126.1 (sextet, J = 0.1 Hz), 116.2 (dd, J_1 = 0.3 Hz, J_2 = 0.8 Hz), 106.1 (d, J = 0.1 Hz), 45.5 (s), 27.6 (s); UV (hexane) λ_{max} 222 nm (log ϵ 2.634), 354 (0.422); mass spectrum (70 eV), m/e (relative intensity) 321 ($M^{\cdot+}$, ^{34}S, 3.8), 320 ($M^{\cdot+}$ + 1, ^{32}S, 8.7), 319 ($M^{\cdot+}$, ^{32}S, 58.8), 255 (100). Anal. Calcd for $C_{10}H_7F_6NO_2S$: C, 37.63; H, 2.21. Found: C, 37.69; H, 2.24.

The reaction was repeated at 180 °C for 72 h to give **19** (8.2%) as the only product isolated.

(c) FVP at 250 °C, 300 °C, 400 °C, and 650 °C. The azide was subjected to FVP at 250 °C and the reaction mixture separated in the usual way on a silica gel column to give **5d** (91.1%) and 3,5-bis(trifluoromethyl)-10-thia-1-azabicyclo[5.3.0]deca-2,4,6-triene 10,10-dioxide (**19**) (3.6%).

The pyrolysis was repeated at 300 °C which gave 3,3',5,5'-tetrakis(trifluoromethyl)azobenzene (**20**) (0.2%) [identical with authentic sample[7]], azide (8.7%), **19** (48.9%), and 6,8-bis(trifluoromethyl)-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**6d**) (6.3%): mp 101–102 °C; IR (KBr) 3320 (m), 1680 (m), 1370 (s), 1340 (s), 1305 (s), 1275 (s), 1225 (m), 1205 (m), 1160 (s), 1120 (s), 905 (s), 870 cm^{-1} (m); NMR ($CDCl_3$) δ 7.84 (s, 1 H), 7.72 (s, 1 H), 7.09 (bs, 1 H, exchanges with D_2O, NH) 3.64 (t, 2 H, J = 4.0 Hz), 3.43 (t, 2 H, J = 4.0 Hz); mass spectrum (70 eV), m/e (relative intensity) 322 $M^{\cdot+}$ + 1, ^{34}S, 0.3), 321 ($M^{\cdot+}$, ^{34}S, 3.0), 320 ($M^{\cdot+}$ + 1, ^{32}S, 7.0), 319 ($M^{\cdot+}$, ^{32}S, 53.9), 234 (100). Anal. Calcd for $C_{10}H_7F_6NO_2S$: C, 37.63; H, 2.21. Found: C, 37.62; H, 2.21.

The pyrolysis was repeated at 350 °C which gave **20** (trace) and **19** (35.9%).

The pyrolysis at 400 °C gave **20** (trace) and **19** (16.2%), while pyrolysis at 450 °C and 650 °C gave only small quantities of very polar polymeric materials that were shown to contain sulfur and nitrogen by a sodium fusion test.

FVP of 3,5-Bis(trifluoromethyl)-10-thia-1-azabicyclo-[5.3.0]deca-2,4,6-triene 10,10-Dioxide (19). 3,5-Bis(trifluoromethyl)-10-thia-1-azabicyclo[5.3.0]deca-2,4,6-triene 10,10-dioxide (**19**) was subjected to FVP at various temperatures with the following results: at 300 °C only **19** was recovered quantitatively; at 350 °C only **19** (81.6%) was obtained; at 375 °C **19** (27.7%) and a trace of sultam **6d** were isolated; at 400 °C **19** (11.3%) was isolated together with a trace of sulfur dioxide extrusion products as detected by GC/MS (4 ft × 2 mm ID, 5% Apiezon M on Gas Chrom Q, 100–120 mesh, He carrier, 30 mL/min, programmed run, 100 °C 2 min, 20 °C/min, 250 °C 15 min). At 500 °C only tars were formed from which no identifiable products could be isolated.

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Registry No. **5a**, 70555-51-0; **5b**, 70555-56-5; **5c**, 88106-84-7; **5d**, 93427-32-8; **6a**, 70555-52-1; **6b**, 70555-57-6; **6c**, 93427-19-1; **6d**, 93427-34-0; **7a**, 93427-12-4; **7b**, 93427-17-9; **7c**, 93427-23-7; **7d**, 93427-35-1; **9a**, 70555-53-2; **9b**, 70555-58-7; **9c**, 82260-13-7; **10a**, 70555-54-3; **10a** (picrate), 70555-55-4; **12**, 70555-59-8; **13**, 70555-60-1; **14**, 93427-20-4; **15**, 93427-21-5; **16**, 27508-85-6; **17**, 93427-27-1; **18**, 93427-26-0; **19**, 93427-33-9; **20**, 75092-04-5; $Cu(NO_3)_2$, 3251-23-8; β-(3,5-dimethylphenyl)ethyl alcohol, 62343-67-3; β-(3,5-dimethylphenyl)ethyl bromide, 93427-11-3; β-(3,5-dimethylphenyl)ethanesulfonyl chloride, 88106-98-3; cyclopropyl bromide, 4333-56-6; 3,5-lutidine, 591-22-0; 3,5-dichloro-β-phenethyl alcohol, 93427-13-5; 3,5-dichlorobromobenzene, 19752-55-7; ethylene oxide, 75-21-8; 3,5-dichloro-β-phenethyl bromide, 93427-14-6; sodium 3,5-dichloro-β-phenethylsulfonate, 93427-15-7; 3,5-dichloro-β-phenethylsulfonyl chloride, 93427-16-8; 3,5-dimethoxy-β-phenethyl bromide, 37567-80-9; sodium 3,5-dimethoxy-β-phenethylsulfonate, 93427-18-0; 3,5-dimethoxy-β-phenethylsulfonyl chloride, 88106-99-4; 3,5-dimethoxybenzyl cyanide, 13388-75-5; 2-nitro-3,5-dimethoxybenzyl cyanide, 93427-22-6; 3-methoxy-β-phenethyl bromide, 2146-61-4; sodium 3-methoxy-β-phenethylsulfonate, 93427-24-8; 3-methoxy-β-phenethylsulfonyl chloride, 93427-25-9; 1,3-bis(trifluoromethyl)-5-bromobenzene, 328-70-1; 3,5-bis(trifluoromethyl)-β-phenethyl alcohol, 93427-28-2; 3,5-bis(trifluoromethyl)-β-phenethyl bromide, 93427-29-3; sodium 3,5-bis(trifluoromethyl)-β-phenethylsulfonate, 93427-30-6; 3,5-bis(trifluoromethyl)-β-phenethylsulfonyl chloride, 93427-31-7; 3,3',5,5'-tetrakis(trifluoromethyl)azoxybenzene, 64857-70-1; 3,3',5,5'-tetrakis(trifluoromethyl)hydrazobenzene, 75092-05-6.

Supplementary Material Available: Full experimental data for the syntheses of sulfonyl azides and sulfonamides (Tables II and III) and of compound **20** (11 pages). Ordering information is given on any current masthead page.