in intensity of a signal characteristic of the substrate was monitored at measured intervals by taking the mean of multiple sweeps (concentrations for NMR kinetics were 0.33–0.50 M).

The results are given in Table III.

For some of the azides, kinetics were also determined by following the volume of nitrogen evolved. This technique allowed more dilute solutions (~0.02 M) to be used than in the NMR method. There was no difference in the rate constants obtained that could not be attributed to solvent effect, and the plots were linear in all cases through one or more half-lives.

(*E*)-1-Bromo-2-(but-2-en-2-yl)benzene.[28] *o*-Bromoacetophenone (91 g) was treated with a small excess of ethylmagnesium bromide; the solvent (ether) was removed, and the residual liquid was boiled with benzene and a trace of iodine until 8.5 mL of water had been collected in a Dean–Stark trap. Distillation of the mixture at 0.1 mmHg yielded 85 g (88%) with a constant boiling point of 70 °C. Its IR spectrum was virtually a band-for-band match with that reported for (*E*)-(but-2-en-2-yl)benzene[29] and was distinctly different from that of the *Z* isomer of the latter and of the structural isomer, (but-1-en-2-yl)benzene. Anal. Calcd for $C_{10}H_{11}Br$: C, 56.60; H, 5.70. Found: C, 56.69; H, 5.55.

(*E*)-1-Azido-2-(but-2-en-2-yl)benzene (11).[28] The foregoing bromo compound (10.0 g) was converted to the Grignard reagent by reaction with magnesium and 100 mL of tetrahydrofuran (THF) and was then added to a solution of *p*-toluenesulfonyl azide in THF at 0 °C, and the mixture was allowed to stand for 12 h. It was then mixed with a solution of 20 g of *p*-toluenesulfonamide and 30 g of NaOH in 200 mL of water and steam-distilled. The distillate was extracted with several portions of ether, and the extracts were dried ($CaCl_2$) and distilled; 4.3 g (52%) of **11**, bp 34–44 °C (0.03 mmHg) was collected: IR (film) 2120, 1290 cm^{-1}, otherwise the same as that of (*E*)-(but-2-en-2-yl)benzene[29] and its *o*-bromo derivative. Anal. Calcd for $C_{10}H_{11}N$: C, 69.34; H, 6.40. Found: C, 69.48; H, 6.42.

Thermolysis[28] of 11. A solution of 1.0 g of **11** in 60 mL of decalin was heated at 175 °C until gas evolution ceased (ca. 1 h); 117 mL was collected (calcd 106 mL). The cooled solution was then extracted with 100 mL of 8% HCl and with concentrated HCl. The concentrated HCl extract was made basic with aqueous NaOH and then extracted with several portions of ether; evaporation of the ether after drying (Na_2SO_4) and treatment with charcoal left 0.40 g (43%) of nearly white solid, which was sublimed at 100 °C (0.01 mmHg) and recrystallized twice from petroleum ether (bp 60–75 °C): 0.20 g (22%); mp 104–107 °C (reported mp 108 °C); IR identical with that of authentic 2,3-dimethylindole.[30]

Registry No. **7**, 96308-06-4; **8**, 959-16-0; **9**, 96308-07-5; **10a**, 96308-08-6; **10b**, 96308-09-7; **10c**, 96308-10-0; **10d**, 96308-11-1; **10e**, 96308-12-2; **11**, 96308-16-6; PhN_3, 622-37-7; *o*-$N_3C_6H_4CH_2CH{=}CH_2$, 78480-04-3; *o*-$N_3C_6H_4CH_2CHO$, 78480-05-4; (*Z*)-*o*-$N_3C_6H_4OCH{=}CHCH_3$, 78480-07-6; PhCHO, 100-52-7; $PhCOCH_3$, 98-86-2; CH_3-*p*-$C_6H_4COCH_3$, 122-00-9; CH_3O-*p*-$C_6H_4COCH_3$, 100-06-1; Cl-*p*-$C_6H_4COCH_3$, 99-91-2; O_2N-*p*-$C_6H_4COCH_3$, 100-19-6; *o*-$N_3C_6H_4CH_2Br$, 31553-17-0; *o*-$N_3C_6H_4CH_2NH_2$, 96308-13-3; CO_2, 124-38-9; *o*-$N_3C_6H_4NHCOPh$, 96308-14-4; PhCOCl, 98-88-4; *o*-$N_3C_6H_4CHO$, 16714-25-3; *o*-$H_2NC_6H_4CH{=}NOH$, 3398-07-0; *anti*-*o*-$O_2NC_6H_4CH{=}NOH$, 4836-00-4; $PhCH_2NH_2$, 100-46-9; (*E*)-*o*-$BrC_6H_4C(CH_3){=}CHCH_3$, 96308-15-5; *o*-$BrC_6H_4COCH_3$, 2142-69-0; *p*-$CH_3C_6H_4SO_2N_3$, 941-55-9; *N*-(2-azidophenyl)-phthalimide, 92159-39-2; potassium phthalimide, 1074-82-4; 2,3-dimethylindole, 91-55-4.

(28) We are indebted to Dr. L. O. Krbechek for this preparation.
(29) Cram, D. J. *J. Am. Chem. Soc.* **1952**, *74*, 2137.
(30) Marion, L.; Oldfield, C. W. *Can. J. Res., Sect. B* **1947**, *25*, 1.

Solution and Flash Vacuum Pyrolysis of Some 2,6-Disubstituted β-Phenethylsulfonyl Azides and of β-Styrenesulfonyl Azide

Rudolph A. Abramovitch,* Albert O. Kress, Kutten S. Pillay,† and W. Marshall Thompson

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

Received November 19, 1984

Solution thermolysis of 2,6-dichloro-β-phenethyl- and 2,6-dimethyl-β-phenethylsulfonyl azide leads to the formation of the corresponding 5,8-disubstituted 3,4-dihydro-2,1-benzothiazine 2,2-dioxides resulting from a 1,2-chlorine and -methyl shift, respectively, in the intermediates. No insertion into the phenethyl side chain, or into the side-chain methyl group in the 2,6-dimethyl case, was detected. Attempted cyclization of ethenesulfonanilides to 2,1-benzothiazine 2,2-dioxide failed. The orientation of the dichlorosultam was established unambiguously by its FVP to 4,7-dichloroindoline and by the synthesis of an authentic sample. Solution thermolysis of β-styrenesulfonyl azide gave only hydrogen abstraction (**32**) and solvent insertion (**33**) products, but FVP gave indole, phenylacetonitrile, and phenylacetylene.

The solution and flash vacuum pyrolysis of β-phenethylsulfonyl azide[1] and β-arylpropanesulfonyl azides[2] have been reported. Sultams and ring transformation products were obtained, particularly with the phenethyl compounds. The first step involved the formation of a sulfonylnitrene which then added intramolecularly to give a benzaziridine intermediate. This either gave the expected sultam or underwent ring expansion and subsequent transformations on flash vacuum pyrolysis. It was of interest, therefore, to see what would happen if the position ortho to the ethyl side chain were blocked, since the usual sultam could not then be formed. To this end, we studied the solution and flash vacuum thermolysis of β-2,6-dichlorophenethyl- and β-2,6-dimethylphenethylsulfonyl azides. In no case was any intramolecular C–H insertion by the sulfonylnitrene into the ethyl side chain observed.

The azides were synthesized by standard procedures. The corresponding ethyl bromide **1** was converted to the sodium sulfonate **2** with sodium sulfite and then to the sulfonyl chloride **3** with thionyl chloride and DMF. The

† Some of this work was performed at the University of Alabama, University, AL 35486.

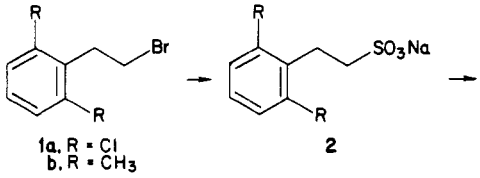
(1) Abramovitch, R. A.; Holcomb, W. D.; Wake, S. *J. Am. Chem. Soc.* **1981**, *103*, 1425.
(2) Abramovitch, R. A.; Kress, A. O.; McManus, S. P.; Smith, M. R. *J. Org. Chem.* **1984**, *49*, 3114.

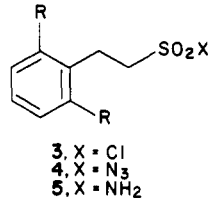
0022-3263/85/1950-2066$01.50/0

Table I. Solution Thermolysis of 4a at Various Temperatures

temp, °C	time, h	yields, % 5a	6a	7	4a
125	72	8.3	tr		64.7
135	36	4.8	25.0		56.3
150	24	7.6	10.4		36.1
185	12	32.9	9.8	14.1	35.5

azides 4 were then prepared from 3 with sodium azide in aqueous acetone.



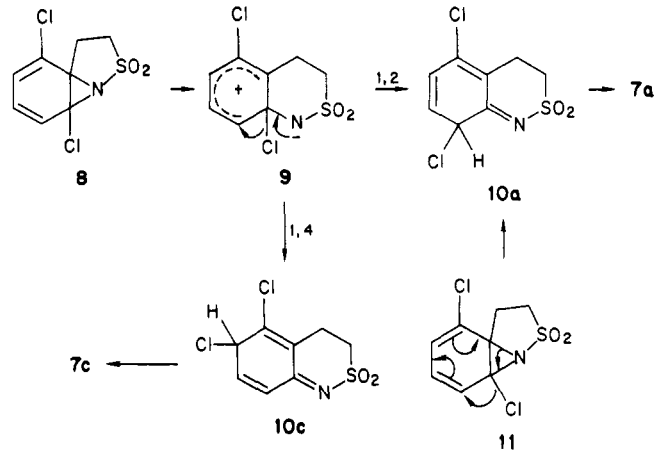


Thermolysis of **4a** in Freon 113 appeared to require more stringent conditions than did that of a β-phenethylsulfonyl azide containing no ortho substituents[1] or only one such substituent (vide infra). In these latter cases, evolution of nitrogen in Freon 113 took place readily at 124–150 °C (see also ref 2). Under those conditions, some decomposition of **4a** (or of **4b**) took place but did not yield sultam. Smooth thermolysis of **4a** did take place at 185 °C while that of **4b** required a temperature of 210 °C for 69 h. This seems to be a function of the solvent used here (Freon 113), for a study[3] of the kinetics of the decomposition of **4a** and **4b** (in which the rate-determining step is the unimolecular elimination of N_2 from the azide) indicates that these decompose at about the same rate at 135 °C in 1-chloronaphthalene as do a large number of other sulfonyl azides, and $\Delta G^{\ddagger}$ values for the decomposition of these compounds are very similar to those of all the others (though $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are appreciably different for **4a** and **4b**: $\Delta H^{\ddagger}_{4a}$ = 36.1 kcal mol^{-1}, $\Delta H^{\ddagger}_{4b}$ = 29.3 kcal mol^{-1}; $\Delta S^{\ddagger}_{4a}$ = 8.2 eu, $\Delta S^{\ddagger}_{4b}$ = −8.2 eu; $\Delta G^{\ddagger}_{4a}$ = 32.6 kcal mol^{-1}; $\Delta G^{\ddagger}_{4b}$ = 32.8 kcal mol^{-1}; $\Delta G^{\ddagger}_{Ph}$ = 32.7 kcal mol^{-1}).[3]

Thermolysis of **4a** at 125–150 °C gave **5a** and **6a**, together with much recovered starting azide. The results are summarized in Table I.

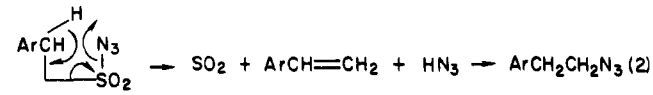
On the other hand, solution thermolysis of **4a** in Freon 113 at 185 °C gave 2,6-dichloro-β-phenethyl azide (**6a**) (9.5%), **5a** (32.7%), and dichloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**7**) (14.1%), in addition to recovered azide (35.5%). Formation of alkyl azides, such as **6a**, from an alkylsulfonyl azide has been observed before[2,4-6] and has been interpreted either as a homolytic cleavage of the sulfonyl azide followed by loss of SO_2 and coupling of alkyl and azide radicals (eq 1) or concerted elimination of HN_3 and SO_2 leading to a styrene followed by addition of the HN_3 (eq 2). The primary sulfonamide **5a** must result from intermolecular hydrogen abstraction by the sulfonylnitrene

Scheme I

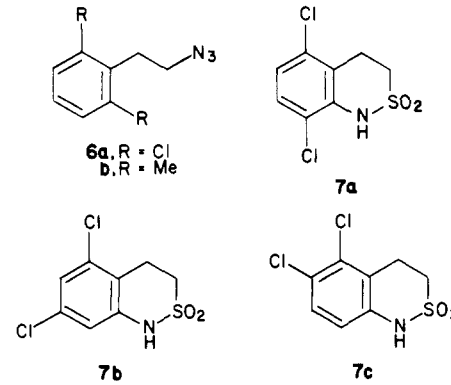


from a molecule of sulfonyl azide since no other source of hydrogen is present.

$$ArCH_2CH_2SO_2N_3 \rightarrow SO_2 + ArCH_2CH_2\cdot + N_3\cdot \xrightarrow{-SO_2} ArCH_2CH_2N_3 \quad (1)$$

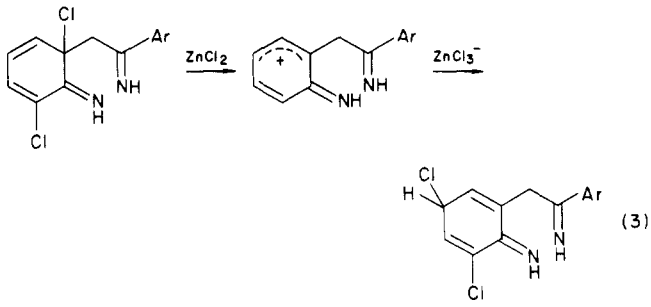


The sultam **7** still contains two chlorine atoms, and its seems reasonable to assume that it results from a migration of *one* chlorine in the intermediate formed. Thus, three



structures **7a–c** are possible for this compound. Chlorine (and other) migrations from ortho positions have been observed in a number of intramolecular cyclizations, notably the Fischer indole synthesis. In the latter case, cyclization of (2,6-dichlorophenyl)hydrazones in the presence of Lewis acid catalysts leads to 5,7-dichloroindoles.[7] On the other hand, fusion of these hydrazones with stannous chloride leads to monodehalogenation and the formation of 7-chloroindoles as one of the products.[8] The halogen migration in the presence of $ZnCl_2$ is believed to involve ionization to an alkyl cation which is then captured by $ZnCl_3^-$[7] (eq 3). On the other hand, the reaction of sulfonylnitrenes with arenes in solution is known to involve addition of the nitrene to the arene to give a benzaziridine followed by heterolytic ring opening to give a dipolar intermediate.[9] On that basis, the initial intramolecular adduct **8** would ring open to **9** which could undergo 1,2- or (less likely, since an antarafacial patahway would be

(3) McManus, S. P.; Smith, M. R.; Abramovitch, R. A.; Offor, M. N. *J. Org. Chem.* **1984**, *49*, 683.
(4) Abramovitch, R. A.; Holcomb, W. D. *J. Chem. Soc. D* **1969**, 1298.
(5) Kress, A. O. Ph.D. Dissertation, Alabama, 1979.
(6) Breslow, D. S. In "Nitrenes"; Lwowski, W., Ed.; Interscience: New York, 1970; pp 245–303.
(7) Carlin, R. B.; Wallace, J. G.; Fisher, E. E. *J. Am. Chem. Soc.* **1952**, *74*, 990. Carlin, R. B.; Larson, G. W. *Ibid.* **1957**, *79*, 934.
(8) Carlin, R. B.; Anoros-Martin, L. *J. Am. Chem. Soc.* **1959**, *81*, 730.
(9) Abramovitch, R. A.; Bailey, T. D.; Takaya, T.; Uma, V. *J. Org. Chem.* **1974**, *39*, 340. Abramovitch, R. A.; Knaus, G. N.; Uma, V. *Ibid.* **1974**, *39*, 1101 and references cited therein.

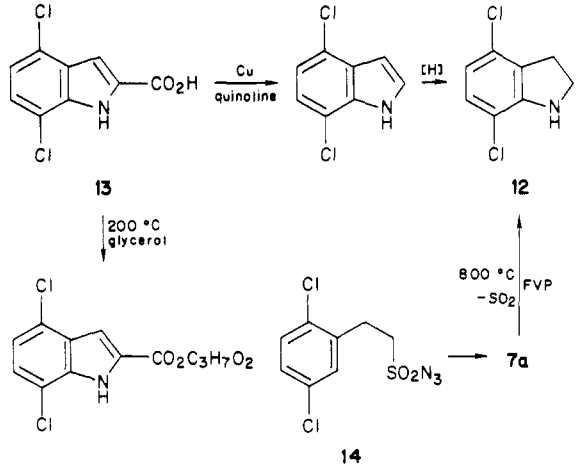


(3)

required in a concerted process) 1,4-halide shift to give **10a** or **10c**, respectively, and thence **7a** or **7c** (Scheme I). A concerted process (**11** → **10a**) is also a possibility. Thus, the orientation of the chlorines in **7** could not be assumed and had to be determined unambiguously. The 1,2 shift also has a precedent in the NIH shift of 1-halobenzene oxides.

The NMR spectrum of **7** showed the presence of two aromatic protons exhibiting ortho coupling (J = 8.82 Hz). This eliminates **7b** from consideration but does not distinguish between **7a** and **7c**. An attempt was made to use shift reagents to decide which was the correct structure. It was obvious, however, that complexation of Eu(fod)$_3$ occurred at the sulfonyl oxygen atoms and not at nitrogen since addition of this shift reagent to a solution of a 3,4-dihydro-2,1-benzothiazine 2,2-dioxide having both C_7 and C_8 free caused no special shift of the C_8 proton, $\Delta\delta$ being of about the same magnitude for C_7H and C_8H. Indeed, addition of 1 equiv of Eu(Fod)$_3$ to a solution of **7** caused both aromatic protons to be shifted downfield by 0.064 ppm.

Structure **7a** was finally confirmed as the product by its flash vacuum pyrolysis at 800 °C to 4,7-dichloroindoline (**12**) (60%), identical with an authentic sample prepared in low yield (10.6%) from the corresponding indole with bis(trifluoroacetoxy)borane.[10] The use of tetra-*n*-butylammonium borohydride[11] led to an even lower yield (1.5%) of **12**. The dichloroindole itself was eventually obtained in 81.0% by decarboxylation of 4,6-dichloroindole-2-carboxylic acid (**13**) with copper powder in quinoline at 195–200 °C. Attempts to decarboxylate the acid by heating it with 5% hydrochloric acid[12] or by FVP at 350–650 °C gave only recovered acid. When the ammonium salt of **13** was heated with glycerol at 200 °C, a good yield of the glyceryl ester of **13** was obtained. FVP of **7a** at 650 °C



(10) Maryanoff, B. E.; McComsey, D. F. *J. Org. Chem.* **1978**, *43*, 2733.
(11) Wakamatsu, T.; Inake, H.; Ogawa, A.; Watanabe, M.; Ban, Y. *Heterocycles* **1980**, *14*, 1441.
(12) Abramovitch, R. A.; Shapiro, D. *J. Chem. Soc.* **1956**, 4589. Abramovitch, R. A. *Ibid.* **1956**, 4953.

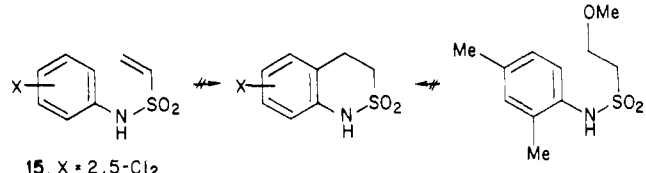
Table II. Attempted Cyclization of 17

reagent	time	temp, °C	product, % 17	product, % 2,4-xylidine
PPA	10 min	140		100
H_2SO_4	2 min	50		100
TFA	12 h	80	100	
TFA	24 h	100	95	tr
TFA	24 h	120	50	50
TFA	24 h	140		100
n-Bu$_3$P	12 h	25	100	
n-Bu$_3$P	24 h	80	100	
Na	24 h	180	100	
FVP		300	93.7	

gave starting sultam quantitatively. The mass spectrum (70 eV) of **7a**, however, was identical with that of the indoline **12**, indicating that the sultam radical cation undergoes fragmentation to the radical cation of **12** prior to entering the analyzer. As expected, addition to Eu(fod)$_3$ to a solution of **12** (complexation must perforce occur at nitrogen here) only leads to very small shifts of the aromatic protons [$\Delta\delta$ (ppm)/equiv of Eu(fod)$_3$]: H_5, 0.059; H_6, 0.069. To make assurance doubly sure an authentic sample of **7a** was prepared by the thermolysis of β-2,5-dichlorophenethylsulfonyl azide (**14**) in Freon 113. Sultam **7a** (40.1%) was obtained together with hydrogen abstraction product (24.1%).

Other attempts to generate dichloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxides (**7**) failed. For example, 2′,5′-dichloroethenesulfonanilide (**15**) and 3′,4′-dichloroethenesulfonanilide (**16**) were prepared from the corresponding aniline and 2-bromoethanesulfonyl chloride followed by reaction with base. Treatment of these with $AlCl_3$ in $(CH_2Cl)_2$ gave only recovered starting material. This is in contrast to the behavior of the carbonyl analogues which cyclize smoothly[13] and agrees with the experience of Loev and Kormendy,[14] who found that ethenesulfonanilide itself did not cyclize with $AlCl_3$ or with polyphosphoric acid. On the other hand, styrenesulfonanilide did give the desired sultam.[14]

To study the conditions under which cyclization might be effected ethenesulfon-2,4-xylidide (**17**) was treated with



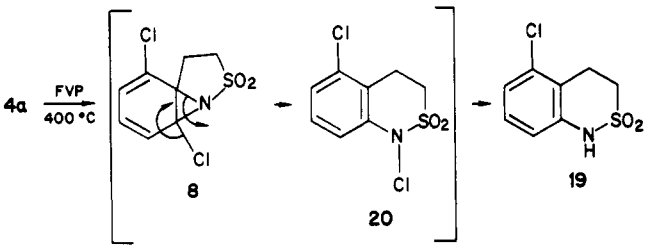
15, X = 2,5-Cl$_2$
16, X = 3,4-Cl$_2$
17, X = 2,4-Me$_2$

18

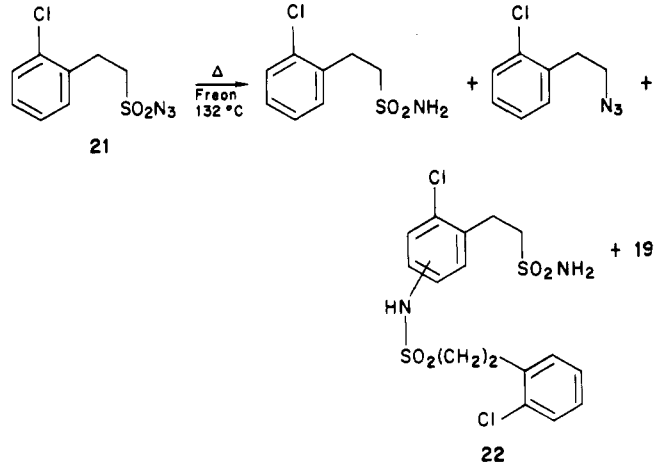
a variety of reagents (Table II). In no case was any cyclization observed; in a few cases hydrolysis to the aniline took place. Similarly, 2-methoxyethanesulfon-2,4-xylidide (**18**) (either from 2-methoxyethanesulfonyl chloride and 2,4-xylidine or from **17** and sodium methoxide) failed to cyclize with a variety of acids (BF_3·OEt_2 at 25–80 °C, $TiCl_4$ at 25–150 °C, $SnCl_4$ at 25–150 °C, and H_2SO_4 at 50–100 °C): the sulfonamide was recovered quantitatively. With H_2SO_4 at 150 °C for 2 min the anilide **18** was completely hydrolyzed.

Flash vacuum pyrolysis of **4a** at 400 °C and 0.5 mmHg (N_2 flow), followed by acid wash and chromatographic workup, gave 5-chloro-3,4-dihydro-2,1-benzothiazepine 2,2-dioxide (**19**) (33.9%). A possible explanation for the difference between the solution and gas-phase behavior could be that in the absence of solvation rearrangement

(13) Mayer, F.; van Zulphen, L.; Phillips, H. *Chem. Ber.* **1927**, *60*, 858.
(14) Loev, B.; Kormendy, M. F. *J. Org. Chem.* **1965**, *30*, 3163.

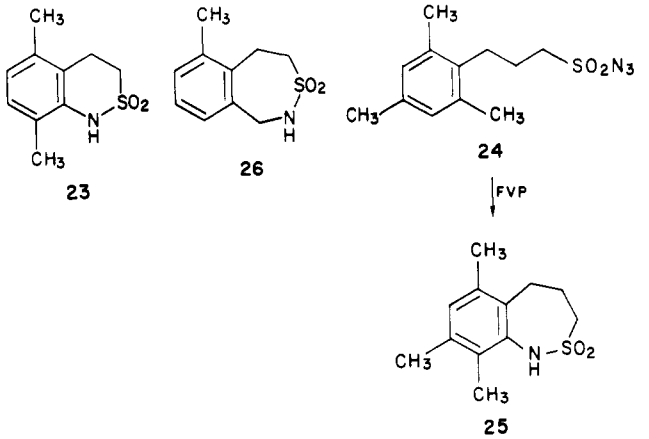


of **8** to the *N*-chloro derivative **20** occurs rather than opening to the dipolar intermediate **9**, and **20** then gets reduced to **19** on workup. The structure of **19** was confirmed by its unambiguous synthesis from 2-chloro-β-phenethylsulfonyl azide (**21**). When the latter was heated in Freon 113 at 132 °C, it gave **19** (4.5%), together with hydrogen abstraction product (12.5%) and 2-chloro-β-phenethyl azide (4.3%). Starting azide (32.1%) was recovered. In addition, a small amount of a compound $C_{16}H_{18}Cl_2N_2O_4S_2$ was isolated. While, at first sight, this might be thought to be a product of dimerization of 2-$ClC_6H_4CH_2CH_2SO_2NH\cdot$, a symmetrical dimer seems ruled out by the mass spectral evidence. Indeed, the mass spectrum (70 eV) of this product shows the expected $M^{+\cdot}$ isotopic pattern for a compound containing two Cl but exhibits no peak at *m/e* 218 (M/2, ^{35}Cl) as might have been expected of a symmetrical hydrazine. The presence of peaks at *m/e* 359–355 suggests loss of SO_2 and NH_3 which would be possible from the cyclization of a side chain $ArCH_2CH_2SO_2NH_2 \rightarrow \overbrace{Ar^+CH_2CH_2}$ under electron impact. Thus, we tentatively assign structure **22** to this product. This would result from an attack of a sulfonylnitrene upon a second molecule of azide in solution followed by decomposition of the latter azide function and hydrogen abstraction.



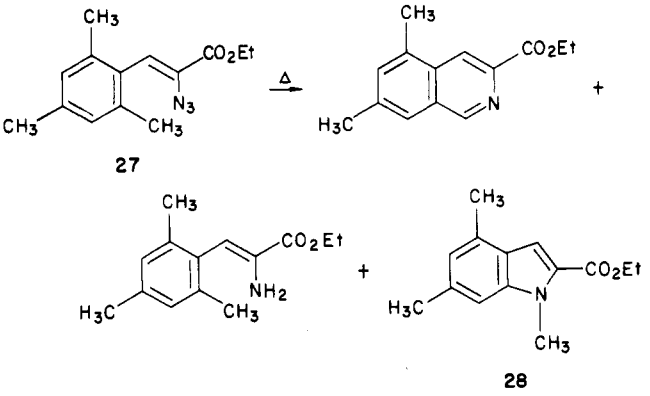
It should be noted that in no case studied here in which both ortho positions were blocked was any insertion of the sulfonylnitrene into the ethyl side chain observed. It would be of interest to study the FVP of β-isopropylsulfonyl azide where competition from addition of the nitrene to the aromatic ring is eliminated, to see whether or not a 4-membered sultam might result under these conditions.

Thermolysis of 2,6-dimethyl-β-phenethylsulfonyl azide (**4b**) in Freon 113 took place conveniently at 210 °C. When the azide was heated in degassed Freon 113 at 135 °C for 165 h, it was recovered almost quantitatively. After 69 h at 210 °C no more azide was left. The products formed were the hydrogen abstraction product **5b** (72.0%) and 5,8-dimethyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**23**) (18.6%). The structure of the latter was assigned on the basis of its NMR [two methyl singlets at δ 2.2 and 2.0, two CH_2 triplets centered at δ 3.5 (CH_2SO_2) and 2.97 ($ArCH_2$), and two aromatic protons at δ 6.77 and 6.64, respectively] and infrared spectrum (ν_{NH} 3190 cm^{-1}) and by analogy with the methyl shift observed with 3-(2-mesityl)propanesulfonyl azide (**24**) which gave **25**.[2] Flash vacuum pyrolysis



of **4b** at 400 °C gave **23** (33.2%). Insertion into the ortho methyl group to give the seven-membered sultam **26** was eliminated from consideration by the absence of a singlet for $ArCH_2N$. Thus, neither eight- nor seven-membered ring sultams are formed from alkylsulfonylnitrenes by intramolecular insertion into an ortho side chain methyl group if competing attack of the aromatic nucleus is possible. Instead, the ortho ring carbon undergoes ipso attack followed by methyl migration to the adjacent ring carbon.

It is worthwhile to contrast this to the recently reported cyclization of *trans*-β-mesityl-α-azidoacrylate (**27**) which gives insertion into the side chain methyl group (isoquinoline formation after dehydrogenation), hydrogen abstraction, and indole ring formation (**28**) involving mi-



gration of the ortho methyl group to nitrogen, and not to the adjacent ring carbon position.[15] It is interesting to speculate on the possible reason for the different behaviors of the vinylnitrene[15] and the alkylsulfonylnitrenes. With the former, the intermediate σ-complex **29** is uncharged and could conceivably undergo a [1,9] (or [1,5]) methyl migration to nitrogen to give aromatic **28** directly, whereas

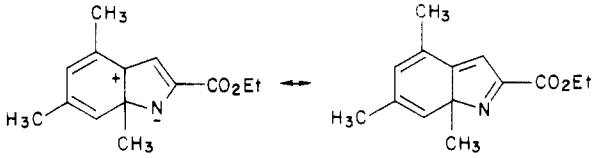
(15) Henn, L.; Hickey, D. M. B.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2189.
(16) (a) Isomura, K.; Kobayashi, S.; Taniguchi, H. *Tetrahedron Lett.* **1968**, 3499. (b) Anderson, D. J.; Hassner, A. *J. Org. Chem.* **1973**, *38*, 2565. (c) Boyer, J. H.; Krueger, W. E.; Mikol, G. L. *J. Am. Chem. Soc.* **1967**, *89*, 5504.
(17) Oliver, J. E.; DeMilo, A. B. *Synthesis* **1975**, 321.
(18) Hartig, S. *J. Prakt. Chem.* **1966**, *33*, 215.
(19) Kharasch, M. S.; May, E. M.; Mayo, F. R. *J. Org. Chem.* **1938**, *3*, 175.
(20) Pappalardo, G.; Vitali, T. *Gazz. Chim. Ital.* **1958**, *88*, 1147.

Table III. Solution Thermolysis of 31

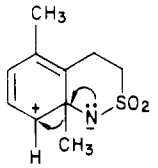
solv	temp, °C	time, h	recovered azide	products,[a] % 32	33[b]
benzene	133	36	tr	56.1	7.3
cyclohexane	134	48	11	29.7	61.9
Freon 113	137	36	38.7	24.9	

[a] Yields based on amount of azide consumed. [b] Authentic samples of **33a**,[17] **33b**,[18] and **32**.[19]

charged intermediate **30** seems to prefer to undergo 1,2-methyl shift to carbon to give **23**.

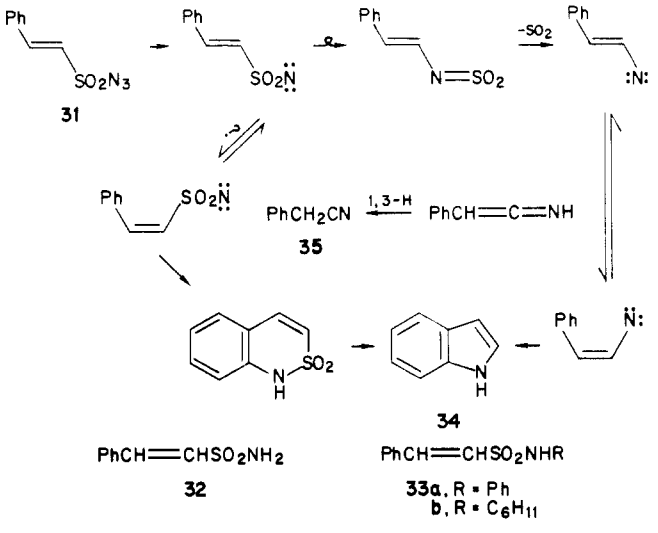


29



30

The kinetics of the decomposition of β-styrenesulfonyl azide (**31**) have been measured,[3] and although the reactivity of this compound was about normal, its olefinic nature and trans geometry could provide alternate reaction pathways. This is indeed the case, for while solution thermolysis gave only hydrogen abstraction (**32**) and solvent insertion products (**33**) (Table III) flash vacuum pyrolysis of **31** resulted in the formation of indole (**34**), phenylacetonitrile (**35**), and, in one case, phenylacetylene (**35**) (Table IV). The indole could arise via a Curtius-type rearrangement giving β-styrylnitrene, which then ring closes, or by a trans–cis isomerization of the sulfonylnitrene, cyclization, and then loss of SO_2. The phenylacetonitrile most probably arises from β-styrylnitrene. Indeed, both **34** and **35** have been isolated (though in different ratios) from the *solution* thermolysis of both *cis*- and *trans*-β-styryl azide **16** (Table IV). The phenylacetylene (**36**) could arise by a radical cleavage (cf. eq 1) or concerted elimination of HN_3 and SO_2 (cf. eq 2).

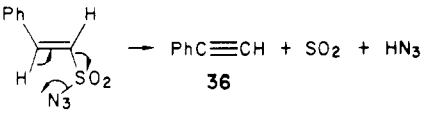


31

34

PhCH=CHSO$_2$NH$_2$ **32**

PhCH=CHSO$_2$NHR **33a**, R = Ph; **b**, R = C_6H_{11}



36

Experimental Section

Sodium 2,6-Dichloro-β-phenethylsulfonate. A solution of 2,6-dichloro-β-phenethyl bromide (41.2 g, 0.163 mol) in 95% ethanol (150 mL) was added to a solution of Na_2SO_3 (26.5 g, 0.210 mol) in water (225 mL) and the mixture boiled under reflux for 24 h. The solution was filtered hot and kept at 5 °C overnight. The white solid which formed was filtered and recrystallized from aqueous ethanol to give sodium 2,6-dichloro-β-phenethylsulfonate (40.6 g, 89.8%) as colorless plates: mp >350 °C; IR (Nujol) 1210 (s), 1200 (s), 1170 (s), 1055 cm^{-1} (s). Anal. Calcd for $C_8H_7Cl_2NaO_3S$: C, 34.67; H, 2.55. Found: C, 34.67; H, 2.52.

2,6-Dichloro-β-phenethylsulfonyl Chloride. To a suspension of the sodium sulfonate (28.5 g, 0.103 mol) in dry benzene (250 mL) were added dry DMF (3.2 mL) and $SOCl_2$ (24.0 g, 0.202 mol), and the mixture was boiled under reflux overnight. The solution was cooled and poured into ice–water (250 mL), the benzene layer separated, and the aqueous layer extracted with ether (3 × 100 mL). The combined organic layers were washed with water (250 mL), dried (Na_2SO_4), and concentrated in vacuo, and the residue was recrystallized from light petroleum (bp 60–80 °C) to give 2,6-dichloro-β-phenethylsulfonyl chloride (29.9 g, 100%) as colorless needles: mp 45–46 °C; IR (Nujol) 1380 (s), 1170 (s), 785 (s), 705 cm^{-1} (s); NMR ($CDCl_3$) δ 7.27 (m, 3 H), 3.75 (m, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 278 (M^{+},$^{37}Cl_3$, 2), 276 (M^{+},$^{37}Cl_2{}^{35}Cl$, 7), 274 (M^{+},$^{37}Cl^{35}Cl_2$, 20), 272 (M^{+},$^{35}Cl_3$, 20), 172 (100). Anal. Calcd for $C_8H_7Cl_3O_2S$: C, 35.12; H, 2.56. Found: C, 35.24; H, 2.61.

2,6-Dichloro-β-phenethylsulfonyl Azide (5, R = Cl). To a solution of the acid chloride (2.9 g, 10.6 mmol) in acetone (30 mL) was added dropwise a solution of NaN_3 (1.07 g, 16.5 mmol) in water (8 mL), and the resulting mixture was stirred for 24 h at room temperature. Most of the acetone was removed in vacuo, and the residue was diluted with water (50 mL) and extracted with ether (3 × 50 mL). The combined ethereal extracts were washed with water (2 × 20 mL), dried ($MgSO_4$), and concentrated in vacuo to give a white solid (3.1 g). This was recrystallized from aqueous ethanol to give the sulfonyl azide (2.9 g, 98.6%): mp 59–59.5 °C; IR (Nujol) 2120 (s), 1355 (s), 1180 (s), 1158 (s), 785 cm^{-1} (s); NMR ($CDCl_3$) δ 7.30 (m 3 H), 3.53 (m, 4 H). Anal. Calcd for $C_8H_7Cl_2N_3O_2S$: C, 34.30; H, 2.52. Found: C, 34.38; H, 2.53.

2,6-Dichloro-β-phenethylsulfonamide. A mixture of the acid chloride (1.0 g, 3.66 mmol) and concentrated NH_4OH (30 mL)

Table IV. FVP of 31 and Thermolysis of β-Styryl Azide

azide	mode of decomp	solv	temp, °C	products,[a] % 34	35	36	other	ref
31	FVP		650	22.2	66.6	6.2		*a*
	FVP		400	25.6	59.9			*a*
trans-PhCH=CHN$_3$	soln	*n*-$C_{16}H_{34}$	287	42.5	42.5			16a
	soln	$C_6H_5CH_3$	110				*b*	16b
	neat		*d*		74			16c
	soln	ligroin	100–105		<2		*c*	16a
cis-PhCH=CHN$_3$	soln	*n*-$C_{16}H_{34}$	287	42.5	42.5			16a
	soln	ligroin	100–105		<2		*c*	16a

[a] This work. [b] 2-Phenylazirine (100%) was the only product reported (trapped as Diels–Alder adduct). [c] 2-Phenylazirine in unspecified yield. [d] Decomposition in the injection port of the gas chromatograph.

was heated to boiling and cooled, and the white precipitate was filtered and recrystallized from benzene to give 2,6-dichloro-β-phenethylsulfonamide (0.8 g, 82.8%): mp 160–161 °C; IR (Nujol) 3340 (s), 3250 (s), 1320 (s), 1145 (s), 1135 (s), 780 cm^{-1} (s); NMR (Me_2SO-d_6) δ 7.5 (m, 3 H), 7.1 (b s, 2 H, exchanges with D_2O, NH), 3.4 (m, 4 H); mass spectrum (70 eV), *m/e* (relative intensity) 257 (s), 255 (s), 253 ($M^{+\cdot}$,$^{35}Cl_2$, 6), 172 (100). Anal. Calcd for $C_8H_9Cl_2NO_2S$: C, 37.81; H, 2.57. Found: C, 37.84; H, 3.57.

Thermolysis of 4 (R = Cl) in Freon 113 at 185 °C: Typical Procedure. The azide (1.0 g, 3.57 mmol) in dry Freon 113 (75 mL) was placed into a Fisher-Porter tube, and the solution was degassed and heated at 185 °C for 12 h. The tube was cooled, the contents were removed, the tube was washed with hot ethyl acetate (2 × 20 mL), and the combined solution and washings were concentrated in vacuo to give a brown oil (994.2 mg). This was chromatographed on a silica gel column (1.8 × 15.0 cm) to give the following fractions. 2,6-Dichloro-β-phenethyl azide (**6a**) (75.9 mg, 9.8%) [eluted with hexane and then hexane–benzene (8:1, v/v)] as an amost colorless oil: IR (film) 2100 cm^{-1} (m). 2,6-Dichloro-β-phenethylsulfonyl azide (**4**, R = Cl) (355.2 mg, 35.5%) [eluted with hexane–benzene (1:1, v/v) and then with benzene–ether (3:1, v/v)] was identical with starting azide. 5,8-Dichloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**7a**) (127.1 mg, 14.1%) [eluted with benzene–ether (3:1, v/v)]: mp 166–167 °C [(from hexane–benzene (3:1, v/v)]; IR (KBr) 3280 (s), 1320 (s), 1150 cm^{-1} (s); NMR ($CDCl_3$) δ 7.27 (d, 1 H, *J* = 8.82 Hz), 7.06 (d, 1 H, *J* = 8.82 Hz), 6.92 (b s, 1 H, exchanges with D_2O, NH), 3.55 (t, 2 H, *J* = 5.38 Hz), 3.37 (t, 2 H, *J* = 5.38 Hz). Anal. Calcd for $C_8H_7Cl_2NO_2S$: C, 38.11; H, 2.80. Found: C, 38.28; H, 2.89. 2,6-Dichloro-β-phenethylsulfonamide (**5**, R = Cl) (298.9 mg, 32.9%) [eluted with benzene–ether (1:1, v/v) and then ether] was identical with an authentic sample.

Flash Vacuum Pyrolysis of 4 (R = Cl) at 400 °C. The azide (2.0 g, 7.14 mmol) was pyrolyzed[1] at a column temperature of 400 °C, with the preheater at 70 °C, the inlet at 130 °C, and the exit at 150 °C, using nitrogen (0.5–0.7 mm pressure) as the carrier gas. The products were washed from the cold finger (dark brown mass) with methanol, the solution was filtered and evaporated, and the residue was dissolved in ethyl acetate (100 mL). This solution was extracted with 2 N HCl (3 × 25 mL) and then with water (2 × 20 mL), dried ($MgSO_4$), and evaporated under reduced pressure to give a dark brown semisolid (fraction A, 848 mg). The aqueous acidic extract was brought to pH 9 with sodium carbonate solution and extracted with ethyl acetate (3 × 35 mL). The extract was washed with water, dried ($MgSO_4$), and evaporated in vacuo to give a reddish semisolid, B (43 mg). Fraction A was chromatographed on a silica gel column (25 g). Elution with benzene gave a dark brown semisolid (339 mg) which showed infrared absorptions at 3250 (s br), 1570 (s), 1325 (s), and 1160 (s) cm^{-1}. This fraction was rechromatographed on a neutral alumina column (10 g). Elution with benzene gave a reddish oil (168 mg) which was distilled [150 °C (0.1 mm)] to give a colorless oil: IR (neat) 3300 (m, v br), 1570 (s), 1340 (m), 1180 (s), 1140 (s), 1110 (s), 750 (s) cm^{-1}. Further elution with 5–20% ethyl acetate in benzene gave 5-chloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**19**) (121 mg), identical with an authentic sample (vide infra). Further elution with 50–100% dichloromethane in benzene and 20–100% ethyl acetate in dichloromethane gave more 5-chloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (353 mg). Elution with 5–20% methanol in ethyl acetate gave a mixture (51 mg) which, on recrystallization from benzene, gave more **19**.

2-Chloro-β-phenethylsulfonyl azide (21) was prepared in 43% overall yield from 2-chlorophenylacetic acid using the same sequence as for 2,6-dichloro-β-phenethylsulfonyl azide: IR (film) 210 (s), 1370 (s), 1190 (s), 1160 (s), 755 cm^{-1} (s); NMR ($CDCl_3$) δ 7.45 (m, 4 H), 3.57 (m, 4 H). Anal. Calcd for $C_8H_8ClN_3O_2S$: C, 39.11; H, 3.28; N, 17.10. Found: C, 39.06; H, 3.35; N, 17.36.

Thermolysis of 21 in Freon 113. A solution of azide **21** (2.25 g, 9 mmol) in Freon 113 (25 mL) was degassed by a freeze–pump–thaw cycle (three times) at 0.05 mmHg. It was then heated with stirring in a Fisher-Porter tube at 132 °C for 65 h. The dark mass on the sides of the tube was extracted with ethyl acetate and combined with the Freon solution, filtered, and evaporated under reduced pressure to give a dark brown viscous oil (1.723 g). This was chromatographed on a neutral alumina (50-g) column. Elution with light petroleum gave 2-chlorophenethyl azide as an oil (48 mg, 4.3%): IR (neat) 2100 (s), 1585 (w), 1560 (w), 1470 (s), 1050 (s), 760 (s) cm^{-1}. Elution with 50% benzene in light petroleum and then benzene gave the unreacted sulfonyl azide (723 mg, 32.1%). Elution with 50% ethyl acetate in methylene chloride gave a mixture of products (83.4 mg). Elution with ethyl acetate gave a fraction (181.3 mg) which was rechromatographed on a silica gel (5 g) column to give 2-chloro-β-phenethylsulfonamide (168 mg, 12.3%): mp 103.5–104.5 °C (from benzene); IR (Nujol) 3360 (s), 3310 (s), 3260 (m), 3220 (s), 1330 (s), 1310 (s), 1155 (s), 1150 cm^{-1} (s); NMR (Me_2SO-d_6) δ 7.30 (m, 4 H, ArH), 6.55 (b s, NH_2), 3.29 (b s, 4 H, H_α and H_β); mass spectrum (70 eV), *m/e* 221 ($M^{+\cdot}$,^{37}Cl), 219 ($M^{+\cdot}$,^{35}Cl), 184, 154, 141, 140, 139, 138 (100%), 127, 125, 120, 104, 103, 102, 101. Anal. Calcd for $C_8H_{10}ClNO_2S$: C, 43.74; H, 4.59; N, 6.38. Found: C, 44.13; H, 4.56; N, 6.41.

Elution with 5–10% methanol in ethyl acetate gave a fraction (184.4 mg) which showed two spots on the plate. This was rechromatographed on a silica gel column (5 g) and gave, on elution with methylene chloride, 5-chloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (65 mg, 4.8%): mp 174.5–175 °C (from benzene); IR (Nujol) 3280 (s), 1333 (s), 1153 cm^{-1} (s); NMR (Me_2SO-d_6) δ 7.15 (m, aromatic), 6.9 (b s, NH, 3.9 (m, H_3, H_4); mass spectrum (70 eV), M/*e* (relative intensity) 219 ($M^{+\cdot}$,^{37}Cl, 11), 217 ($M^{+\cdot}$,^{35}Cl, 29), 155 (7), 154 (17), 153 (21), 152 (48), 151 (3), 118 (29), 117 (100), 116 (14), 91 (25), 90 (13), 89 (19). Anal. Calcd for $C_8H_8ClNO_2S$: C, 44.14; H, 3.70; N, 6.44. Found: C, 44.44; H, 3.73; N, 6.30. Identical with sample obtained from the FVP.

Elution of the silica gel column with 1% methanol in methylene chloride gave a semisolid (98.9 mg) which, on recrystallization from benzene containing a small amount of methanol, afforded a solid tentatively assigned structure **22**: mp 164–165 °C; IR (Nujol) 3330 (m), 3250 (m), 3200 (m), 1330 (s), 1315 (s), 1190 (s) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 440 ($M^{+\cdot}$,$^{37}Cl_2$, 5) 438 ($M^{+\cdot}$,$^{37}Cl^{35}Cl$, 18), 436 ($M^{+\cdot}$,$^{35}Cl_2$, 26), 359 (8), 358 (6), 357 (25), 356 (7), 355 (31), 249 (9), 247 (18), 236 (14), 234 (33), 222 (12), 186 (20), 169 (16), 168 (17), 167 (10), 166 (26), 155 (29), 154 (21), 153 (60), 152 (24), 141 (42), 140 (22), 139 (100), 138 (24), 119 (27), 103 (100), 97 (36), 95 (26), 85 (36), 83 (37), 81 (27), 77 (55), 71 (57), 69 (45). Anal. Calcd for $C_{16}H_{18}Cl_2N_2O_4S_2$: C, 43.94; H, 4.15; N, 6.41. Found: C, 44.37; H, 4.16; N, 6.33.

Methyl (2,5-Dichlorophenyl)acetate. To a solution of (2,5-dichlorophenyl)acetonitrile (12.3 g, 66.2 mmol) in dry methanol (100 mL) was added concentrated H_2SO_4 (10 mL), and the mixture was boiled under reflux for 72 h. It was poured into water (300 mL) and extracted with $CHCl_3$ (3 × 100 mL). The extracts were dried ($MgSO_4$), the solvent was evaporated in vacuo, and the residue was distilled to give methyl (2,5-dichlorophenyl)acetate (13.9 g, 96.0%): bp 87 °C (0.10 mm); IR (film) 1760 cm^{-1} (s); NMR ($CDCl_3$) δ 7.30 (m 3 H), 376 (s, 5 H, $ArCH_2$ and OCH_3). Anal. Calcd for $C_9H_8Cl_2O_2$: C, 49.34; H, 3.68. Found: C, 49.32; H, 3.68.

2,5-Dichloro-β-phenethyl Alcohol. To a suspension of $LiAlH_4$ (3.0 g, 79.0 mmol) in dry ether (150 mL) was added dropwise a solution of the acetate (11.0 g, 50.0 mmol) in dry ether (25 mL), and the mixture was boiled under reflux overnight, cooled in ice, and hydrolyzed by the sequential addition of water (3 mL), 15% aqueous NaOH (3 mL), and water (12 mL). The inorganic salts were filtered and washed well with ether, and the filtrate was dried ($MgSO_4$) and evaporated in vacuo, and the residue was distilled to give 2,5-dichloro-β-phenethyl alcohol (9.4 g, 98.8%): bp 91 °C (0.10 mm); IR (film) 3300 cm^{-1} (br s, OH); NMR ($CDCl_3$) δ 7.30 (m, 3 H), 3.87 (t, 2 H, *J* = 7.0 Hz), 2.95 (t, 2 H, *J* = 7.0 Hz), 2.70 (b s, 1 H, exchanges with D_2O, OH) (lit.[21] bp 121–122 °C (3 mm)).

Sodium 2,5-Dichloro-β-phenethylsulfonate. Prepared from sodium sulfite (6.6 g, 52.0 mmol) in water (70 mL) and 2,5-dichloro-β-phenethyl bromide[21] (10.1 g, 39.9 mmol) in 95% ethanol (45 mL) it gave the sodium sulfonate (5.5 g, 50.0%) (from water): mp >345 °C; IR (KBr) 1620 (m), 1245 (s), 1215 (s), 1180 (s), 1145 cm^{-1} (s); NMR (D_2O) δ 7.27 (m, 3 H), 3.02 (s, 4 H). Anal. Calcd for $C_8H_7Cl_2NaO_2S$: C, 34.68; H, 2.55. Found: C, 33.13; H, 2.61.

2,5-Dichloro-β-phenethylsulfonyl Chloride. The sodium sulfonate (3.1 g, 11.3 mmol) in dry benzene (40 mL) and dry DMF (0.5 mL) and $SOCl_2$ (3.5 g, 29.4 mmol) gave, as before, the sulfonyl

(21) Berkovic, S. *J. Org. Chem.* **1955**, *20*, 1322.

chloride (2.7 g, 86.4%): bp 95–100 °C (0.25 mm); mp 34–36 °C; IR (film) 1460 (s), 1375 (s), 1160 (s), 1095 (s), 1045 cm^{-1} (s); NMR ($CDCl_3$) δ 7.25 (s, 3 H), 3.95 (m, 2 H), 3.45 (m, 2 H). Anal. Calcd for $C_8H_7Cl_3O_2S$: C, 35.12; H, 2.58. Found: C, 35.21; H, 2.66.

2,5-Dichloro-β-phenethylsulfonyl Azide (14). To a solution of sulfonyl chloride (1.0 g, 3.7 mmol) in acetone (20 mL) was added a solution NaN_3 (0.5 g, 7.7 mmol) in water (5 mL), and the mixture was stirred at room temperature overnight. Most of the acetone was removed in vacuo; the residue was diluted with water (20 mL) and extracted with ether (3 × 20 mL). The extracts were dried ($MgSO_4$) and passed through a column of basic alumina (1.5 cm × 5.0 cm). Elution with ether and evaporation of the ether in vacuo gave the azide as a colorless oil (0.7 g, 68.3%): bp 90–95 °C (0.025 mm); IR (film) 2140 (s), 1375 (s), 1165 cm^{-1} (s); NMR ($CDCl_3$) δ 7.36 (s, 3 H), 3.68 (m, 2 H), 3.29 (m, 2 H); mass spectrum (70 eV), *m/e* (relative intensity) 283 ($M^{+\cdot}$ $^{37}Cl_2$, 4), 281 ($M^{+\cdot}$ $^{37}Cl^{35}Cl$, 23), 279 ($M^{+\cdot}$ $^{35}Cl_2$, 33), 102 (100).

2,5-Dichloro-β-phenethylsulfonamide. The sulfonyl chloride (1.0 g, 0.4 mmol) in 95% ethanol (10 mL) and concentrated ammonium hydroxide (5 mL) gave the sulfonamide (72.4 mg, 77.8%): mp 162–163 °C (from benzene); IR (KBr) 3580 (s), 3520 (m), 1215 (s), 1180 (s), 1065 cm^{-1} (s). Anal. Calcd for $C_8H_9Cl_2NO_2S$: C, 37.81; H, 3.57. Found: C, 37.77; H, 3.61.

Thermolysis of 14 in Freon 113 at 185 °C. A solution of **14** (240.0 mg, 0.86 mmol) in Freon 113 (70 mL) was degassed and heated at 185 °C for 24 h in a Fisher-Porter tube. The tar which separated was extracted with hot $CHCl_3$ (2 × 25 mL), and the extracts were combined with the Freon solution and evaporated in vacuo to give a dark brown oil. This was chromatographed on a silica gel column (1.8 × 15.0 cm) to give 5,8-dichloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**7a**) (86.7 mg, 40.1%) [eluted with benzene and then with benzene–ether (3:1, v/v)], identical with the sultam obtained form the solution thermolysis of (**4**, R = Cl) at 185 °C, and 2,5-dichloro-β-phenethylsulfonamide (**5**, R = Cl) (52.5 mg, 24.1%) [eluted with benzene–ether (1:1, v/v)], identical with the authentic sample.

2′,5′-Dichloroethenesulfonanilide (15). To a solution of 2-bromoethanesulfonyl chloride (4.14 g, 20.0 mmol) and 2,5-dichloroaniline (3.24 g, 20.0 mmol) in ether (100 mL) was added dropwise pyridine (3.16 g, 40.0 mmol) in ether (20 mL), and the mixture was stirred overnight at room temperature. The ethereal solution was washed with 2 N HCl (3 × 50 mL) for 30 min, and insoluble impurities were extracted with ether (3 × 50 mL). The aqueous solution was acidified and extracted with ether (3 × 50 mL). The combined extracts were dried ($MgSO_4$) and evaporated in vacuo, and the residue recrystallized from hexane–benzene (3:1, v/v) to give 2′,5′-dichloroethenesulfonanilide (**15**) (0.5 g, 10.7%): mp 106–108 °C; IR (KBr) 3270 (s), 1340 (s), 1155 cm^{-1} (s); NMR ($CDCl_3$) δ 7.60 (d, 1 H, $J_{1',3'}$ = 2.4 Hz, H_1), 7.32 (d, 1 H, $J_{2',3'}$ = 8.8 Hz, H_2), 7.07 (dd, 1 H, $J_{1',3'}$ = 2.4 Hz, $J_{2',3'}$ = 8.8 Hz, H_3), 6.85 (b s, 1 H, exchanges with D_2O, NH), 6.61 (dd, 1 H, J_{BX} = 8.8 Hz, J_{AX} = 16 Hz, H_X), 6.32 (dd, 1 H, J_{AX} = 16 Hz, J_{AB} = 0.7 Hz, H_A), 6.02 (dd, 1 H, J_{BX} = 9 Hz, J_{AB} = 0.7 Hz, H_B). Anal. Calcd for $C_8H_7Cl_2NO_2S$: C, 38.11; H, 2.80. Found: C, 38.04; H, 2.90.

3′,4′-Dichloroethenesulfonanilide (16). Prepared (11.3%) as above from 3,4-dichloroaniline: mp 101–102 °C; IR (KBr) 3240 (s), 1330 (s), 1150 cm^{-1} (s); NMR ($CDCl_3$) δ 7.39 (d, 1 H, $J_{2',3'}$ = 8.8 Hz, H_2), 7.29 (d, 1 H, $J_{1',3'}$ = 2.4 Hz, H_1), 7.02 (dd, 1 H, $J_{1',3'}$ = 2.6 Hz, $J_{2',3'}$ = 8.8 Hz, H_3), 6.72 (b s, 1 H, exchanges with D_2O, NH), 6.59 (dd, 1 H, J_{BX} = 9 Hz, J_{AX} = 16 Hz, H_X), 6.29 (d, 1 H, J_{AX} = 16 Hz, H_A), 6.02 (d, 1 H, J_{BX} = 9 Hz, H_B). Anal. Calcd for $C_8H_7Cl_2NO_2S$: C, 38.11; H, 2.80. Found: C, 38.26; H, 2.83.

Attempted Cyclization of 15. To a solution of **15** (0.1 g, 0.4 mmol) in dichloroethane (10 mL) was added anhydrous $AlCl_3$ (0.3 g, 2.0 mmol) in one portion, and the mixture was stirred overnight at room temperature. It was cooled in ice and hydrolyzed with 2 N HCl. The solution was extracted with ether (3 × 10 mL), and the ethereal extracts were dried ($MgSO_4$) and evaporated in vacuo. Analysis of the residue showed that no reaction had taken place.

4,7-Dichloroindole. To a solution of 4,7-dichloroindole-2-carboxylic acid[20] (**13**) (4.41 g, 19.2 mmol) in dry quinoline (50 mL) was added freshly prepared Cu powder (2.0 g), and the stirred mixture was heated to 195–200 °C for 1 h. It was cooled in an ice bath, acidified with 2 N HCl, and extracted with ether (3 × 25 mL). The ethereal extracts were dried ($MgSO_4$) and evaporated in vacuo, and the residue was distilled to give a forerun of colorless oil (0.77 g), bp 53–55 °C (0.025 mm), and then 4,7-dichloroindole (2.91 g, 81.5%) as a colorless oil which solidified on standing: bp 70–72 °C (0.025 mm); mp 38–39 °C; IR (film) 3460 (s), 1490 (s), 1415 (s), 1330 (s), 1170 (s), 1065 (s), 920 cm^{-1} (s); NMR ($CDCl_3$) δ 8.4 (b s, 1 H, exchanges with D_2O, NH), 7.2 (t, 1 H, *J* = 2.7 Hz).

4,7-Dichloroindoline (12). To a solution of the indole (0.93 g, 5.0 mmol) in 1 M boron hydride–tetrahydrofuran complex (10 mL), cooled to 0 °C under an atmosphere of dry N_2, was added dropwise trifluoroacetic acid (10 mL). The mixture was stirred for 30 min at 0 °C, and then water (1 mL) was added. The solution was stirred for 15 min more, and most of the THF and TFA was removed in vacuo. The residue was treated with 10% aqueous NaOH (35 mL) and then with water (50 mL) and extracted with ether (4 × 25 mL). The ethereal extracts were washed with 2 N HCl (3 × 10 mL), dried ($MgSO_4$), and evaporated in vacuo, and the residue was distilled to give 4,7-dichloroindole (0.74 g, 79.6%) as a colorless oil that solidified on standing: bp 70–72 °C (0.025 mm). The acid washings were basified and extracted with ether (3 × 20 mL). The ethereal extracts were dried ($MgSO_4$), and the solvent was evaporated in vacuo to give 4,7-dichloroindoline (**12**) (0.10 g, 10.6%) as a colorless oil that was pure as indicated by GLC: bp 64–65 °C (0.05 mm); IR (film) 3420 (s), 1620 (s), 1470 (s), 1295 (s), 1140 cm^{-1} (s); NMR ($CDCl_3$) δ 7.0 (d, 1 H, *J* = 9.0 Hz), 6.6 (d, 1 H, *J* = 9.0 Hz), 3.9 (b s, 1 H, exchanges with D_2O, NH), 3.7 (t, 2 H, *J* = 7.0 Hz), 3.9 (t, 2 H, *J* = 7.0 Hz). Anal. Calcd for $C_8H_7Cl_2N$: C, 51.0; H, 3.75. Found: C, 51.12; H, 3.77.

Reduction of the indole with tetra-*n*-butylammonium borohydride gave **12** but only in 1.5% yield.

FVP of 5,8-Dichloro-3,4-dihydro-2,1-benzothiazine 2,2-Dioxide (7a) at 800 °C. 5,8-Dichloro-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**7a**) (62.7 mg, 0.25 mmol) was subjected to FVP under the following conditions: sublimation temperature, 160 °C; pyrolysis temperature, 800 °C; pressure, 0.025 mm. After the mixture was cooled, the product was washed off the cold finger with ether. The ethereal solution was evaporated in vacuo to give a light brown oil which was distilled to give 4,7-dichloroindoline (**12**) (31.9 mg, 68.3%) as a colorless oil, identical with an authentic sample: bp 64–65 °C (0.05 mm). GC/MS analysis showed the presence of a trace of 4,7-dichloroindole.

Sodium 2,6-Dimethyl-β-phenethylsulfonate (2b). Prepared from 2,6-dimethyl-β-phenethyl bromide (**1b**) (7.0 g) in 95% ethanol (35 mL) and sodium sulfite (5.4 g) in water (45 mL) (6.2 g, 79.5%): mp >360 °C; IR (Nujol) 1610 (m), 1200 (s), 1168 (s), 1055 cm^{-1} (s). Anal. Calcd for $C_{10}H_{13}NaO_3S$: C, 50.84; H, 5.55. Found: C, 51.00; H, 5.50.

2,6-Dimethyl-β-phenethylsulfonyl Chloride (3, R = Me). **2b** (5.2 g) in dry benzene (75 mL) with dry DMF (1 mL) and $SOCl_2$ (5.2 g) gave **3** (R = Me) (4.4 g, 85.0%): mp 71.5–72.5 °C; IR (Nujol) 1368 (s), 1170 (s), 782 (s), 725 cm^{-1} (s); NMR ($CDCl_3$) δ 6.96 (m, 3 H), 3.45 (m, 4 H), 2.33 (s, 6 H, CH_3); mass spectrum (70 eV), *m/e* (relative intensity) 234 ($M^{+\cdot}$ ^{37}Cl, 8), 232 ($M^{+\cdot}$ ^{35}Cl, 21), 119 (100). Anal. Calcd for $C_{10}H_{13}ClO_2S$: C, 51.61% H, 5.63. Found: C, 51.66% H, 5.65.

2,6-Dimethyl-β-phenethylsulfonyl Azide (4, R = Me). To a solution of (**3**, R = Me) (2.0 g, 8.6 mmol) in acetone (20 mL) was added a solution of NaN_3 (0.9 g, 13.0 mmol) in water (5 mL), and the mixture was stirred for 24 h at room temperature. Workup as usual gave the azide (**4**, R = Me) (1.8 g, 87.3%): mp 55.5–56 °C (aqueous EtOH); IR (Nujol) 2130 (s), 1350 (s), 1340 (s), 1325 (s), 1185 (s), 1150 cm^{-1} (s); NMR ($CDCl_3$) δ 6.97 (m, 3 H), 3.27 (m, 4 H), 2.37 (s, 6 H, CH_3). Anal. Calcd for $C_{10}H_{13}N_3O_2S$: C, 50.19; H, 5.48. Found: C, 50.20; H, 5.48.

2,6-Dimethyl-β-phenethylsulfonamide (5, R = Me). The sulfonyl chloride (234 mg, 1.0 mmol) in concentrated ammonium hydroxide (5 mL) gave the amide (201 mg, 94%): mp 156–156.5 °C; IR (Nujol) 3320 (s), 3220 (s), 1320 (s), 1130 cm^{-1} (s); mass spectrum (70 eV), *m/e* (relative intensity) 214 ($M^{+\cdot}$ + 1, 5), 213 ($M^{+\cdot}$, 30), 117 (100). Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.31; H, 7.09. Found: C, 56.25; H, 7.08.

Attempted Thermolysis of 2,6-Dimethyl-β-phenethylsulfonyl Azide in Freon 113. At 210 °C. A solution of 2,6-dimethyl-β-phenethylsulfonyl azide (360 mg) in Freon 113 (10 mL) was degassed (three freeze–dry–thaw cycles) and thermolyzed at 210 °C for 69 h. The Freon solution was decanted, and the thermolysis tube was washed with ether (the dark brown material

was not soluble). The ether washings were combined with the Freon and evaporated under reduced pressure to give a pale yellow thick oil (165 mg) which solidified on standing. It was recrystallized from benzene to give 2,6-dimethyl-β-phenethylsulfonamide, identical with an authentic sample.

The dark brown semisolid in the thermolysis tube was treated with hot ethyl acetate, filtered to remove black insoluble solid, and evaporated under reduced pressure to give a dark brwon resin (150 mg): IR (neat) 3240 (m), 1315 (s), 1145 (s), 1130 (s) cm^{-1}. This mixture was chromatographed on neutral alumina (6 g) and eluted with methylene chloride and ethyl acetate to give 2,6-dimethyl-β-phenethylsulfonamide (65.6 mg). Elution with 5% methanol in ethyl acetate gave a fraction (58.9 mg) which was recrystallized from benzene to give 5,8-dimethyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**23**): mp 180.5–182.0 °C (from benzene); IR (Nujol) 3190 (s), 1320 (s), 1145 (s), 1130 (s), 745 cm^{-1} (s); NMR ($CDCl_3$) δ 6.77, 6.64 (d, 2 H), 3.50 (t, 2 H, CH_2SO_2, J = 7 Hz), 2.97 (t, 2 H, $ArCH_2CH_2$, J = 7 Hz), 3.37 (s, 1 H, NH, D_2O exchangeable), 2.19 (s, 3 H), 2.08 (s, 3 H, CH_3); mass spectrum (70 eV), m/e (relative intensity) 211 ($M^{+\cdot}$, 12), 197 (s), 147 (33), 146 (79), 144 (17), 132 (41), 131 (52), 130 (52), 129 (33), 121 (16), 120 (100), 119 (18), 118 (19), 117 (31), 115 (24), 105 (14), 91 (32), 77 (25). Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.87; H, 6.16. Found: C, 56.92; H, 6.22.

At 136 °C. Only starting azide was recovered after heating for 64 h.

Flash Vacuum Pyrolysis of 2,6-Dimethyl-β-phenethylsulfonyl Azide at 400 °C. 2,6-Dimethyl-β-phenethylsulfonyl azide (325 mg, 1.4 mmol) was placed in the reservoir of the pyrolysis apparatus and pyrolyzed at a column temperature of 400 °C, with the preheater temperature at 75 °C, the inlet at 130 °C, and the exit at 250 °C. The initial pressure was 0.001 mmHg before pyrolysis. During the pyrolysis the pressure was 0.04–0.05 mmHg. No carrier gas was used. The cold finger was cooled with liquid nitrogen. The pyrolysis took 5 h. During the pyrolysis some decomposition of the azide occurred in the inlet reservoir itself as shown by the change in color of the azide. After the pyrolysis, a dark brown mass (51 mg) remained in the inlet reservoir which was not investigated further. A pale yellow solid was condensed near the exit in the receiver (57 mg) and near the inlet in the pyrolysis tube (37 mg). Both of these fractions were combined and recrystallized from benzene to give 5,8-dimethyl-3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**23**): mp 181–182 °C (sublimes at 70 °C at 0.05 mm). A dark brown semisolid condensed on the cold finger was dissolved in methanol, treated with activated charcoal, and filtered. The solvent was removed to give a yellow semisolid (35 mg) which showed no infrared absorptions for $-SO_2N<$ group at 1300–1340 and 1140–1180 cm^{-1} but showed absorptions at 3400 (w, br), 1000 (m, v br), 1095 (s), and 1030 (m) cm^{-1}.

***trans*-β-Styrenesulfonyl Azide.** This was prepared (69.9% yield) as usual from the chloride (Aldrich): mp 31.5–33 °C (from light petroleum, bp 30–60 °C); IR (KBr) 2140 (s), 1360 (vs), 1185 (vs), 1145 cm^{-1} (vse; NMR ($CDCl_3$) δ 7.7–7.4 (m, 6 H, ArH and ArCH), 6.83 (d, 1 H, J = 15.4 Hz, $CHSO_2$). Anal. Calcd for $C_8H_7N_3O_2S$: C, 45.92; H, 3.37. Found: C, 45.93; H, 3.37.

Thermolysis of *trans*-β-Styrenesulfonyl Azide. In Freon 113. The azide (483.6 mg, 2.3 mmol) in dry Freon 113 (50 mL) was heated at 157 °C for 36 h. Chromatography on silica gel gave unchanged azide (187.3 mg, 38.7%), mp 32–33.5 °C, and *trans*-β-styrenesulfonamide (63.7 mg, 24.9%), mp 142–142.5 °C, identical with an authentic sample.[19]

The results of the thermolysis in benzene and in cyclohexane are summarized in Table III.

FVP at 650 °C. The products from the pyrolysis of azide (1.39 g) were separated by column chromatography on silica gel to give the following. Unchanged azide (74.8 mg, 5.4%): mp 32–33.5 °C. Phenylacetylene (39.8 mg, 6.2%): bp 50–55 °C (20 mm); IR (film) 3320 (s), 2210 cm^{-1} (w); NMR (CCl_4) δ 7.6–7.2 (m, 5 H, ArH), 3.13 (s, 1 H, ≡CH); identical with a commercial sample (Aldrich Chem. Co.). A mixture of indole and phenylacetonitrile resolved into its components by preparative liquid chromatography on silica gel using CH_2Cl_2 as eluent. Indole (163.4 mg, 22.2%): mp 52–54 °C; identical with an authentic sample (IR, NMR). Phenylacetonitrile (490.1 mg, 66.6%): bp 76–78 °C (2 mm); IR (film) 2250 cm^{-1} (vs); NMR (CCl_4) δ 7.22 (s, 5 H, ArH), 3.68 (s, 2 H, CH_2); identical with an authentic sample.

Acknowledgment. We thank the National Science Foundation (CHE 78-04805 and CHE-8313525) for support of this work.

Registry No. **1a**, 40173-94-2; **1b**, 79927-86-9; **2a**, 96129-58-7; **2b**, 96129-75-8; **3** (R = Cl), 88106-97-2; **3** (R = Me), 88106-96-1; **4** (R = Cl), 88106-83-6; **4** (R = Me), 88106-82-5; **5** (R = Cl), 96129-59-8; **5** (R = Me), 96129-76-9; **6a**, 96129-60-1; **7a**, 96129-61-2; **12**, 96129-78-1; **13**, 96129-74-7; **14**, 96129-69-0; **15**, 96129-71-4; **16**, 96129-72-5; **19**, 96129-62-3; **21**, 96129-63-4; **22**, 96129-79-2; **23**, 96129-77-0; **31**, 80639-78-7; **32**, 64984-09-4; **33a**, 13719-47-6; **33b**, 13719-46-5; *trans*-PhCH=CHN_3, 18756-03-1; 2-chlorophenethyl azide, 96129-64-5; 2-chloro-β-phenethylsulfonamide, 96129-65-6; 5-chloro-3,4-dihydro-2,1-benzothiazine-2,2-dioxide, 96129-62-3; methyl (2,5-dichlorophenyl)acetate, 96129-66-7; (2,5-dichlorophenyl)acetonitrile, 3218-50-6; 2,5-dichloro-β-phenethyl alcohol, 1875-87-2; sodium 2,5-dichloro-β-phenethylsulfonate, 96129-67-8; 2,5-dichloro-β-phenethyl bromide, 40173-98-6; 2,5-dichloro-β-phenethylsulfonyl chloride, 96129-68-9; 2,5-dichloro-β-phenethylsulfonamide, 96129-70-3; 2-bromoethanesulfonyl chloride, 54429-56-0; 2,5-dichloroaniline, 95-82-9; 3,4-dichloroaniline, 95-76-1; 4,7-dichloroindole, 96129-73-6.

Novel Porphyrins from Copper(II)-Mediated Cyclizations of 1′,8′-Dimethyl-a,c-biladiene Salts: Mechanism of the Cyclization Reaction

Kevin M. Smith* and Ohannes M. Minnetian

Department of Chemistry, University of California, Davis, California 95616

Received November 6, 1984

Copper(II)-mediated cyclizations of the 1′,8′-dimethyl-a,c-biladiene **8** under various conditions afford the expected porphyrin **7**, along with γ-methyl- (**9**), γ-(dialkylamino)- (**10** and **11**), 6-formyl- (**12**), and γ-formylporphyrins (**13**). Carbon-13-enriched a,c-biladienes (**14** and **15**) were used to establish the origins of the γ carbons, γ substituents, and γ-formyl groups; possible mechanistic pathways for the formation of porphyrins by copper(II)-mediated cyclizations of 1′,8′-dimethyl-a,c-biladiene salts are proposed.

The cyclization of a,c-biladiene salts to give porphyrins can be accomplished under a variety of conditions. 8′-Bromo-1′-methyl- (**1**) and 1′-methyl-8′-unsubstituted-a,c-biladiene dihydrobromides (**2**) yield metal-free porphyrins

0022-3263/85/1950-2073$01.50/0